Chemistry = a branch of science which treats of the
composition of substances, their changes + the laws
governing these changes

Valence = an element which combines with H in
proportion of one atom to one atom
Bivalent Combines as one to two

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Cohesion = attraction of particles for each other

Force = action of one body upon another to produce change or arrest motion

Energy = capacity of ~~the~~ body for doing work

Crystals = solid substances bounded by plane surfaces - symmetrically arranged by a

Amorphous = solid substances having no crystalline structure

Heat = is a result of the motion of molecules

Latent Heat = that heat which converts solids to liquids & liquids to gases which
is not indicated by a thermometer

Distillation = conversion of a liquid into gas, or gas into liquid

Boiling point = highest point any liquid can be heated under one atmospheric pressure

Specific Heat = heat required to raise a substance a certain number of degrees as compa
with heat required to raise an equal weight of water the same number of d

Weight = a quantity of mutual attraction between the earth + the object

Specific Weight = is water at 15°C = 59 F.

Specific Gravity = weigh equal volume of water & the liquid + divide the weight of liquid by the

Porosity = having space between the particles.

Adhesion = surface ~~attraction~~ of liquids for solids

Diffusion = gradual passage of one liquid or gas into another.

Colloids = substances not passing thro membranes in process of dialysis

Dialysis = diffusion when 2 liquids are separated by a porous diaphragm
or Osmose

Absorption = the taking up of a liquid or solid into the pores of a

Elements = all substances which cannot be divided into more simple forms (67 in

Compounds = substances capable of being divided or subdivided

Chemical Affinity = a force by which elements unite + form compounds -

Molecules = smallest particle of matter capable of existing in a free state

Atom = " " " " of entering into a compound

Elementary substance = one which the atoms composing its molecules are alike

Compound " = one which the molecules contains atoms of different kinds

Affinity = the attraction of atoms forming molecules

Atomic weight = weight of an atom of element as compared with 1 atom of H

Molecular weight = combined weight of ~~atoms~~ atoms forming molecules

Analysis = substances broken up into elements or group
so that they may be recognized

Synthesis - uniting bodies together to form
more complex substances

Basic substances - have chemical properties opposed to ac

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MANUAL
OF
CHEMISTRY.

A GUIDE TO LECTURES AND LABORATORY WORK FOR BEGINNERS IN CHEMISTRY. A TEXT-BOOK SPECIALLY ADAPTED FOR STUDENTS OF MEDICINE, PHARMACY, AND DENTISTRY.

BY
W. SIMON, PH.D., M.D.,
PROFESSOR OF CHEMISTRY IN THE COLLEGE OF PHYSICIANS AND SURGEONS OF BALTIMORE,
IN THE MARYLAND COLLEGE OF PHARMACY, AND IN THE
BALTIMORE COLLEGE OF DENTAL SURGERY.

FIFTH EDITION, THOROUGHLY REVISED.

WITH FORTY-FOUR ILLUSTRATIONS
AND
EIGHT COLORED PLATES, REPRESENTING SIXTY-FOUR CHEMICAL REACTIONS.

PHILADELPHIA:
LEA BROTHERS & CO.
1895.

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PREFACE TO THE FIFTH EDITION.

THE steadily increasing demand for this Manual has stimulated the author to prepare this new edition with great care and with due consideration of the needs of the student. The many changes and additions made were necessitated not only by the general advance of science, but also because of the desire of the author to bring this work in complete harmony with the new Pharmacopœia.

The orthography recommended by the chemical section of the American Association for the Advancement of Science has not been fully adopted, for the reasons that neither the leading chemical journals nor the United States Pharmacopœia use this spelling, and that it would be unwise to have the student confronted with two different systems of orthography.

As heretofore, the subject has been divided into seven parts each one of which contains so much of the matter under consideration as is believed to be necessary for a fair understanding of the subject. At the same time care has been taken to place in the foreground all facts and data which are of direct interest to the physician, pharmacist, and dentist, and to exclude, as far as is compatible with the presentation of a comprehensive view of chemistry, those portions which are of restricted interest only.

In the first part the fundamental properties of matter are considered briefly, and to such an extent as is necessary for an understanding of chemical phenomena.

The second part treats of those principles of chemistry which are the foundation of the science, and enters briefly into a discussion of theoretical views regarding the atomic constitution of matter. Though the author prefers to present these theories to his classes at the proper times during the course of lectures, he does not deem it desirable to have them scattered throughout the work, believing it better to assemble them compactly in print, so that the student may be able to study them after having acquired some knowledge of chemical phenomena.

The third and fourth parts are devoted to the consideration of the non-metallic and metallic elements and their compounds. While the periodic law furnishes a most admirable basis for a scientific classification of elements, yet their consideration according to a *strict* adherence to periodicity does not seem advisable in this book. For this reason the old classification of metals and non-metals, organic and inorganic compounds, has been retained, since experience has shown it to be well adapted to the instruc-

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tion of beginners in chemistry. All our classifications of either natural objects or phenomena are imperfect, because Nature does not draw those distinct lines of demarcation which we adopt as necessary for our studies. The most simple and natural classification is therefore always to be preferred, even if, as in the above case, the student might derive from it the impression that matter was thus separated into distinct groups.

Of elements, those only are considered which have either intrinsically or in combination a practical interest, or which take an active part in the various chemical changes in nature.

For the special benefit of pharmaceutical and medical students all chemicals mentioned in the last revision of the United States Pharmacopœia are included, and when of sufficient interest they are fully considered.

The fifth part is devoted to analytical chemistry and will serve the student as a guide in his laboratory work. Qualitative methods are chiefly considered, but a chapter is added giving all official methods for volumetric determinations.

The sixth part treats of organic chemistry. Though it is impossible to include within the limits of this text-book an extended consideration of a branch of chemical science so highly developed, yet it is believed that an intelligent study of this part will familiarize the student with carbon compounds sufficiently to give him a clear understanding of their general character, and a knowledge of the bodies which are most important in medical science.

The seventh and last part, giving some of the principal facts of physiological chemistry, was prepared for the benefit of the medical student in particular. Much new matter has again been added to these chapters, and special care has been taken to mention the most modern methods for chemical examination in clinical diagnosis.

As an aid to laboratory work a number of experiments have been added which may readily be performed by students with a comparatively small outfit of chemical apparatus.

The decimal system has been strictly adhered to in all weights and measures; degrees of temperature are expressed in the same system, the corresponding degrees of Fahrenheit being also mentioned.

Many changes have been made on the plates showing the variously shaded colors of a number of substances and the nature of their reactions. There has also been added a new plate illustrating the chemical behavior of a number of the more important benzene derivatives.

W. S.

BALTIMORE, January, 1895.

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ABBREVIATIONS.

c.c. = Cubic centimeter.
B. P. = Boiling-point.
F. P. = Fusing-point.
Sp. gr. = Specific gravity.
U. S. P. = United States Pharmacopœia.

PRACTICAL CHEMISTRY,
PHARMACEUTICAL AND MEDICAL.

I.

INTRODUCTION.

FUNDAMENTAL PROPERTIES OF MATTER. RESULTS OF THE ATTRACTIONS BETWEEN MASSES, SURFACES, AND MOLECULES.

As the science of Chemistry has for its object the study of the nature of all substances, or of all varieties of matter, it is necessary first to consider some of the properties which belong to every kind of matter, and are known as *essential or fundamental properties.* The fundamental properties of matter having a special interest for those studying chemistry are: *extension, divisibility, gravitation, porosity,* and *indestructibility.*

1. EXTENSION OR FIGURE.

Matter is anything occupying space, and this property is known as *extension.* All bodies, without exception, fill a certain amount of space; they all have length, breadth, and thickness. That portion of matter lying within the surrounding surface of a body is called its *mass.* We distinguish three different conditions of matter, namely: *Solids, Liquids,* and *Gases.* These conditions of matter are known as the three states of aggregation, and we will now consider the peculiarities of matter when existing in either of these states.

Solid state. Solids are distinguished by a self-subsistent figure. A solid substance forms for itself, as it were, a casing in which its smallest particles[1] are enclosed. The question arises, By what means are these particles connected? how are they kept together? No other answer can be given than that the particles themselves attract each other to such an extent that force is necessary to make them alter their relative positions. We see, consequently, that some form of attraction or attractive power is acting between the particles of a solid mass, and we call this kind of attraction *cohesion*, to distinguish it from other forms of attraction.

The external appearance or the figure of solid bodies is various. It may be an irregular or a *natural regular figure*. Of these two forms, only the latter is here of interest, as it includes all the different crystallized substances.

Force may be defined as the action of one body upon another body, or as the action of particles of matter upon other particles either of the same or of another body. Strictly speaking, we may say that force is the cause tending to produce, change, or arrest motion; or it is any action upon matter changing or tending to change its form or position.

In many cases force manifests itself as an attractive power; for instance, in the case of cohesion mentioned above, but also in adhesion, gravitation, etc. Forces often give rise to motion (as in the case of heat and electricity), and also to a great variety of changes in matter. The three different states of aggregation are due to the relative intensity of two opposing forces, one—that of molecular attraction—which tends to draw the molecules together, and a second one—that of heat—which tends to separate the molecules from one another.

Energy of a body is its capacity of doing work, and is measured by the product of the force acting and the distance through which it acts.

Crystals are solid substances bounded by plane surfaces symmetrically arranged according to fixed laws. In explaining the formation of crystals we have to assume that the particles are endowed with the power of attracting one another in certain directions, thereby building themselves up into geometrical forms.

The first condition essential to the formation of crystals is the possibility of free motion of the smallest particles of the matter to be crystallized; in that case only will they be able to attract each other in such a way as to assume a regular shape, or form crystals. Particles of a solid mass can move freely only after they have been transferred to the liquid or gaseous state. There are two different methods of liquefaction, viz., by means of heat (melting), or solution in some suitable agent (dissolving). In the liquid condition thus produced, the smallest particles can follow their own attraction, and unite to form crystals on removal of the cause of liquefaction (heat or solvent).

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[1] It will be shown later that all matter is supposed to consist of smallest particles, which we call molecules.

If two or more (non-isomorphous) substances—for instance, common salt and Glauber's salt—be dissolved together in water, and the solution be allowed to crystallize, the attraction of like particles for one another will be readily noticed by the formation of distinct crystals of common salt alongside of crystals of Glauber's salt; neither do the particles of common salt help to build up a crystal of Glauber's salt, nor the particles of the latter a crystal of common salt. Advantage is taken of this property in separating (by crystallization) solids from each other, when they are contained in the same solution.

Not all matter can form crystals; some substances never have been obtained in a crystallized state, such as starch, gum, glue, etc. A solid substance showing no crystalline structure whatever is called *amorphous*.

Some substances capable of crystallization may be obtained also in an amorphous state (carbon, sulphur). Other substances are capable of assuming different crystalline shapes under different conditions. Thus sulphur, when liquefied by heat, assumes, on cooling, a shape different from the sulphur crystallized from a solution. One and the same substance under the same conditions always assumes the same shape. Substances capable of assuming in solidifying two or more different shapes or conditions, are said to be *dimorphous* and *polymorphous*, respectively. When substances of different kinds crystallize in exactly the same form we call them *isomorphous* (sulphate of magnesium and sulphate of zinc). If two isomorphous substances be contained in one solution, they will crystallize together, and the crystals are made up of particles of both substances.

Characteristic properties of solids. Solid substances show a great variety of properties caused by the differences in the cohesion of the particles (molecules) composing the substances, and accordingly we distinguish between hard and soft, brittle, tenacious, malleable, and ductile substances.

Hardness is that property in virtue of which some bodies resist attempts to force passage between their particles, or which enables solids to resist the displacement of their particles. Diamond and quartz are extremely hard, while wax and lead are comparatively soft.

Brittleness is that property of solids which causes them to be broken easily when external force is applied to them. Glass, sulphur, coal, etc., are brittle.

Tenacity is that property in virtue of which solids resist attempts to pull their particles asunder. Iron is one of the most tenacious substances.

Malleability, possessed by some solids, is the property in virtue of which they may be hammered or rolled into sheets. Gold is so malleable that it may be beaten into sheets so thin that it would require about 300,000 laid upon one another to measure one inch.

Ductility is the property in virtue of which some solids may be drawn into wire or thin sheets—as, for instance, copper, iron, and platinum.

Liquid state. The characteristic features of liquids are, that they have no self-subsistent figure; that they consequently require some vessel to hold them; and that they present a horizontal surface. While in a solid substance the smallest particles are held together by cohesion to such an extent that they cannot change their relative position without force, in a liquid this cohesion acts with much less energy and permits of a comparatively free motion of the particles; the repellant and attractive forces nearly balance each other in a liquid. That cohesion is not altogether suspended in a liquid is shown by the formation of drops or round globules, which, of course, consist of a large number of smallest particles. If there were no cohesion at all between these particles of a liquid, drops could not be formed.

The terms semi-solid and semi-liquid substances are used for bodies occupying a position intermediate between true solids and fluids; butter, asphalt, amorphous sulphur, are instances of this kind.

Gaseous state. Matter in the gaseous state has absolutely no self-subsistent figure. Gases fill any vessel or room entirely; the smallest particles show the highest degree of mobility and move freely in every direction. Cohesion is entirely suspended in gases; indeed, the smallest particles exhibit toward each other an infinite repulsion, so that force is necessary to restrain them within any given bounds whatever. It, therefore, follows that gases set up and maintain a pressure against the walls of vessels enclosing them. This characteristic property, possessed by all gases, is known as *elasticity*, or, better, as *tension*, and is so unvarying that a law has been established in relation to it. This law is known as the *Law of Mariotte* (though really discovered by Boyle, of England, in 1661), and may be expressed thus: The volume of a gas is inversely as the pressure; the density and elastic force are directly as the pressure and inversely as the volume. For instance: If a vessel contains one cubic foot of a gas under a pressure of ten pounds, the volume will be reduced to

of Mariotte

one-half, one-tenth, or one-hundredth of one cubic foot, if the pressure be increased to 20, 100, or 1000 pounds respectively. On the contrary, the gas will expand to 2, 10, or 100 cubic feet, if the pressure is reduced to 5, 1, or one-tenth pound respectively. Vapors, produced by evaporation of liquids or solids, have the same properties as gases.

2. DIVISIBILITY.

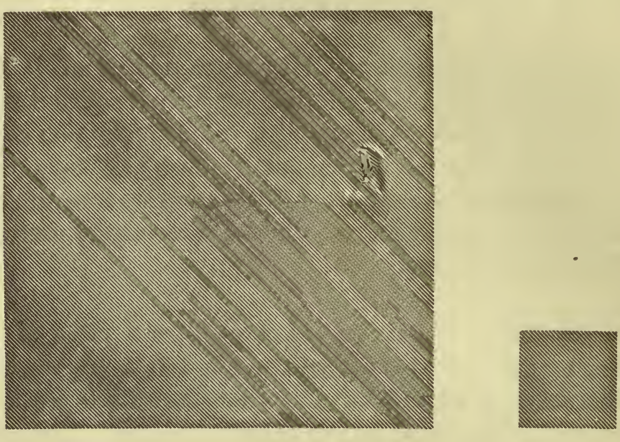
Mechanical comminution. All matter admits of being subdivided into smaller particles, and this property is called divisibility. The processes by which we accomplish the comminution of a solid substance may be of a mechanical nature, such as cutting, crushing, grinding, but beside these modes of subdivision we have other agents or causes by which matter may be divided into smaller particles, and one of these agents is heat.

Action of heat on matter. Let us take a piece of ice and convert it, by means of mortar and pestle, into a very fine powder. When the smallest particle of this finely powdered ice is placed under the microscope and heat applied, we shall observe that it becomes liquid, thus proving that it was capable of further subdivision, that it consisted of smaller particles, which have now by the action of heat become movable. By further applying heat to the liquid particle of water we may convert it into a gas or vapor, which will escape into the air, or which we may collect in an empty flask. The flask will be filled completely by this water-gas (or steam) obtained by vaporizing that minute particle of ice-dust. This fact demonstrates that mechanical comminution does not carry us beyond a certain degree of subdivision of matter. That is to say, the smallest fragment of the finest powder still consists of a very large number of much smaller particles. To the smallest particles which compose matter the name molecules has been given.

QUESTIONS.—1. What is matter and what is force? 2. Mention the principal fundamental properties of matter. 3. Mention the three states of aggregation. 4. Describe the characteristic properties of matter in the solid, liquid, and gaseous states. 5. What is cohesion? 6. Give a definition of a crystallized substance. 7. Under what circumstances will matter crystallize? 8. State the difference between amorphous, polymorphous, and isomorphous substances. 9. What is meant by elasticity or tension of gases? 10. State the law of Mariotte.

Molecular theory. The expression molecule is derived from the Latin word *molecula*—a little mass, and means the smallest particle of matter that can exist by itself, or into which matter is capable of being subdivided by physical actions. To explain more fully what is meant by the expression molecule, we will return to the conversion of water into steam.

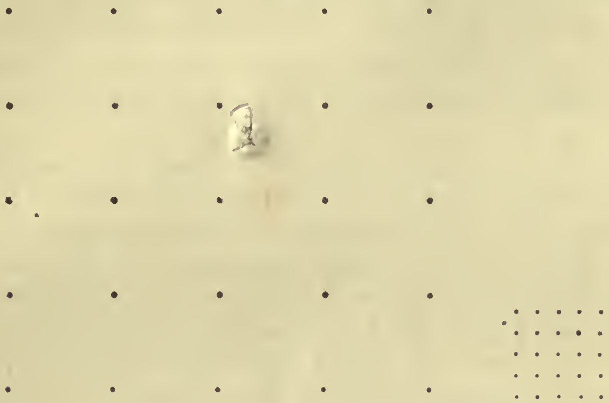
FIG. 1.



When water boils at the ordinary atmospheric pressure it expands about 1800 times, or one cubic inch of water yields about 1800 cubic inches, equal to about one cubic foot of steam. In explaining this fact we have either to assume that the water, as well as the steam, is *homogeneous matter* (Fig. 1), or that the water consisted of small particles of a given size, which now exist in the steam again as such, with the only difference that they are more widely separated from each other (Fig. 2).

Of the many proofs which we have of the fact that the latter assumption is correct, I will mention but one, viz., that the quantities of vapor formed by volatile liquids at any certain temperature above the boiling-point, in close vessels of the same size, are the same, no matter whether the vessel was entirely empty or contains the vapors of one, two, or more other substances. For instance: If we place one cubic inch of water in a flask holding one cubic foot, from which flask the air has been previously removed, and then heat the flask to the boiling-point, the cubic inch of water will evaporate, filling the vessel with steam. Upon now introducing into the flask a second and a third liquid—for instance, alcohol and ether—we find that of each of these liquids exactly the same quantity will evaporate which would have evaporated if these liquids had been introduced into the empty flask.[1] This fact is evidence that there must be small particles of steam which are not in close contact, that there are spaces between these particles which may be occupied by the particles of a second, third, or more substances. To these particles of matter we give the name molecules, and the spaces between them we call intermolecular spaces.

FIG. 2.



We have thus demonstrated the correctness, or, at least, the likelihood of the so-called molecular theory, but the proof given is but one of many. Of these molecules (though individually by far too small to make any impression whatever upon our senses), our conception is so perfect that we have formed an idea of the actual size of these minute particles of matter. Very good reasons lead us to believe that the diameter of a molecule is equal to about $\frac{1}{500000000}$ of one inch, and that one cubic inch of a gas under ordinary conditions contains about one hundred thousand million million millions of molecules.

These figures at first glance appear to be beyond the limit of human conception, but in order to give some idea of the size of these molecules it may be mentioned that if a mass of water as large as a pea were to be magnified to the size of our earth, each molecule being magnified in the same proportion, these molecules would represent balls of about two inches in diameter.

Whilst molecules consequently are exceedingly small particles, yet they are not entirely immeasurable; they are, as Sir W. Thomson says, pieces of matter of measurable dimensions, with shape, motion, and laws of action, intelligible subjects of scientific investigation.

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[1] As each gas, in consequence of its tension, exerts a certain pressure, the pressure in the flask rises with the introduction of every additional gas.

Before leaving the molecular theory, I will mention the *Law* (more correctly, the hypothesis) *of Avogadro*, which may be stated as follows: *All gases or vapors, without exception, contain, in the same volume, the same number of molecules*, provided temperature and pressure are the same. Or, in other words: *Equal volumes of different gases contain, under equal circumstances, the same number of molecules.* The correctness of this law has good mathematical support deduced from the law of Mariotte, many other facts and considerations leading to the same assumption. We shall learn, hereafter, that the law of Avogadro is one of the greatest importance to the science of chemistry.

Motion of molecules. Heat. If we place over a gas-flame a vessel containing a lump of ice of the temperature of 0° C., or 32° F., the ice gradually melts and becomes converted into water; but if we measure with a thermometer the temperature of the water at the moment when the last particle of ice is melted, we still find it at the freezing-point, 0° C. or 32° F. From the position of the vessel over the flame, as well as from the fact that the ice has been liquefied, we know that the vessel and its contents have absorbed heat. Yet vessel and water show the same temperature as before. If the heat of the flame is allowed to continue its action on the ice-cold water, the thermometer will soon indicate a rapid absorption of heat until it reaches 100° C. or 212° F. Then the water begins to boil and escapes in the form of steam, but the temperature again remains stationary until the last particle of water has disappeared.

There must be, consequently, some relation between the state of aggregation of a substance and that agent which we call heat. It was the heat which liquefied the ice, it was the heat which converted the liquid water into steam or gaseous water. Yet the water, having absorbed considerable heat during the process of melting, shows a temperature of 0° C. (32° F.), and the steam also having absorbed large quantities of heat, shows 100° C. (212° F.), the temperature of boiling water. A certain amount of heat has consequently been lost or at least hidden. What has become of it?

According to our present theory, *heat is a result of the motion of molecules*. All molecules of any substance are in a constant vibratory motion, and the velocity or amplitude of this molecular motion determines the degree of what we call heat.

An increase of heat is equal to an increase of the vibratory motion of the molecules and a decrease in temperature is caused by slower motion. The transfer of heat is a transfer of the motion of some particles to other particles.

One of the effects of increased heat is in nearly all cases an increase in volume, or, in other words, all substances expand when heated, and contract on cooling.

Another effect of the application of heat is, as we have just learned, the conversion of solids into liquids, and of liquids into gases. We noticed also the apparent loss of heat during this conversion, and can easily account for it now by saying that a certain amount of vibratory motion or a certain velocity of the molecules (more correctly speaking, perhaps, a certain amplitude of molecular motion) is required to convert solids into liquids and liquids into gases. The molecules of steam vibrate with a much greater velocity than those of water of the same temperature, and the molecules of water move with greater velocity than those of ice of the same temperature. In other words, the different states of aggregation depend on the rapidity of the motion of molecules; and the heat which is necessary to convert solids into liquids and liquids into gases, and which is not indicated by the thermometer, is called *latent heat.*

This latent heat may again be converted into *free heat* (heat capable of being indicated by a thermometer), by reconverting the gas into a liquid, ~~or this latter into a solid~~. In both cases a liberation of heat, which is a transfer of the motion of the molecules upon the surroundings, will be noticed.

Increase of volume by heat. The increase of volume by heat is not alike for all matter. Gases expand more than liquids, liquids more than solids, and of the latter the metals more than most other solid substances. Whilst the expansion of any two or more different solids or liquids is not alike, gases show a fixed regularity in this respect, namely, all gases without exception expand or contract alike when the temperature is raised or lowered an equal number of degrees.

This expansion or contraction of gases is 0.3665 per cent., or $\frac{1}{273}$ of their volume for every degree centigrade; thus 100 volumes of air become 100.3665 volumes when heated 1 degree C., or 136.65 when heated 100 degrees C. This regularity in the expansion and contraction of gases is expressed in the *Law of Charles*, which says: *If the pressure remain constant, the volume of a gas increases regularly as the temperature increases, and decreases as the temperature decreases.* If heat be applied to a gas confined in a closed vessel and be thus prevented from expanding, the increase of heat will manifest itself as pressure, which rises with the same regularity as shown for expansion, viz., 0.3665 per cent. for every degree centigrade.

Melting and boiling. The temperature at which a solid substance is converted into a liquid and this into a gas, is of a certain fixed degree or point for every substance, and the temperatures at which this conversion takes place are known as melting- (fusing-) and boiling-points.

Some forms of matter appear incapable of existing in the three states of aggregation, like water. As yet, we know carbon in the solid state only, and the conversion of some gases, as, for instance, oxygen and hydrogen, into liquids or solids, has been accomplished only recently and in small quantities.

Other substances, again, may assume two, but not the third state. Some substances pass from the solid directly into the gaseous state (ammonium chloride, calomel), and the process of converting a solid into a gas directly, and this back again into a solid, is called *sublimation.*

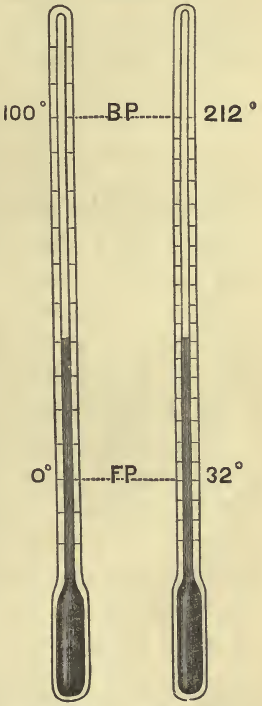
Distillation is the conversion of a liquid into a gas, and the recondensation of the gas into a liquid.

Many liquids, and even some solids, evaporate or assume the gaseous state at nearly all temperatures. Water and ice, mercury, camphor, and many other substances vaporize at temperatures which are far below their regular boiling-points. This fact is to be explained by the assumption that during the rapid vibratory motion of the particles of these masses, some particles are driven from the surface beyond the sphere to which the surrounding molecules exert an attraction, and thus intermingle with the molecules of the surrounding air.

This evaporation, which takes place at various temperatures and at the surface only, is not to be confounded with boiling, which is the rapid conversion of a liquid into a gas at a fixed temperature with the phenomena of ebullition, due to the formation of gas in the mass of liquid. Boiling-point may therefore be defined as the highest point to which any liquid can be heated under the normal pressure of one atmosphere.

Thermometers are instruments indicating different temperatures. Use is made in their construction of the change in volume of different substances by the action of heat. The most common thermometer is the mercury thermometer. This instrument may be easily constructed by partly filling with mercury a glass tube having a bulb at the lower end, and placing it into boiling water. The point to which the mercury rises is marked B. P. (boiling-point), and the tube sealed by fusion of the glass. It is then placed in melting ice, and the point to which the mercury sinks is marked F. P. (freezing-point). The distance between the boiling- and freezing-points is then divided into 100 degrees in the so-called centigrade thermometer, or into 180 degrees in the Fahrenheit thermometer. The inventor of the latter instrument, Fahrenheit, commenced counting not from the freezing-point, but 32° below it, which causes the freezing-point to be at 32°, the boiling-point at 180° above it, or at 212°. (Fig. 3.)

FIG. 3.



Centigrade. Fahrenheit.
Thermometric scales.

Molecular motion. Heat is but one of the results of molecular motion; other results are light, actinism, electricity, and magnetism.

When a body is heated the molecules vibrate quicker, and this molecular motion gives rise to *heat waves* in the assumed surrounding and all-pervading medium called ether; if the heating be continued to a higher degree, the body begins to give out light, which is due to ether waves of shorter length; and if heated yet higher, it gives out not only dark heat waves and *light waves*, but also waves of still shorter length, which make no direct impression on our senses, but which are capable of producing chemical changes in certain substances, and are known as *actinic waves*. Of the character of the molecular motion causing electricity and magnetism we know little, and the various theories which have been advanced in order to explain electrical phenomena are inadequate and insufficient to do so satisfactorily.

Specific heat. Equal weights of different substances require different quantities of heat to raise them to the same temperature. For instance: The same quantity of heat which is sufficient to raise one pound of water from 60° to 70° will raise the temperature of one pound of olive oil from 60° to 80°, or two pounds of olive oil from 60° to 70°. Olive oil consequently requires only one-half of the heat necessary to raise an equal weight of water the same number of degrees. (Specific heat is therefore the heat required to raise a certain weight of a substance a certain number of degrees, compared with X the heat required to raise an equal weight of water the same number of degrees.)

The heat required to raise one pound of water one degree centigrade is usually taken as the unit of comparison. On thus comparing olive oil, we find its specific heat to be $\frac{1}{2}$. If we say the specific heat of mercury is $\frac{1}{32}$, we indicate that equal quantities of heat will be required to raise one pound of water or 32 pounds of mercury one degree, or that the heat which raises one pound of water one degree will raise one pound of mercury 32 degrees.

3. GRAVITATION.

Action of gravitation. Every particle of matter in the universe attracts every other particle; consequently, all masses attract each other, and this attraction is known as *gravitation*. The action of gravitation between the thousands of heavenly bodies moving in the universe is to be considered by astronomy, but some of the phenomena caused by the mutual attraction of the substances composing the earth are of importance for our present consideration.

Such phenomena caused by gravitation are the falling of substances, the flowing of rivers, the resistance which a substance offers on being lifted or carried. A body thrown up into the air or deprived of its support will fall back upon the earth. In this case the mutual attraction between the earth and the substance has caused its fall. It might appear that in this case the attraction was not mutual, but exerted by the earth only; it has been proved, however, by most exact experiments, that there is also an attraction of the falling substance for the earth, but the amount of the force of this attraction is directly proportional to the mass of the bodies, and consequently too insignificant in the above case to be noticed.

The law of gravitation, known as *Newton's law*, may thus be stated: All bodies attract each other with a force directly proportional to their masses and inversely proportional to the squares of their distance apart.

QUESTIONS.—11. What two kinds of divisibility of matter do we distinguish, and by what actions are they accomplished? 12. Explain the term molecule. 13. Mention one of the facts which prove that a gas consists of particles with intervals between them. 14. State the law of Avogadro. 15. Mention the effects produced by increased velocity of the molecules of a mass. 16. Give an explanation of the expressions—latent heat, free heat, and specific heat. 17. Explain the construction of a mercury thermometer. 18. How many degrees of Fahrenheit are equal to 50° C.? 19. How many degrees of centigrade are equal to 167° F.? 20. What is distillation, and what is sublimation?

Weight is an expression used to denote the quantity of mutual attraction between the earth and the body weighed. Here again, the attraction of the substance for the earth is not taken into consideration. All our weighing is a comparison with, or measurement by, some standard weight, such as pound, ounce, gramme, etc.

Specific weight or specific gravity denotes the weight of a body, as compared with the weight of an equal bulk or equal volume of another substance, which is taken as a standard or unit. The word density is frequently used for specific weight, as density means comparative mass. By the density of a body consequently is meant its mass (or quantity of matter) compared with the mass of an equal volume of some body arbitrarily chosen as a standard. The standard or unit adopted for all solids and liquids, if not otherwise stated, is water at a temperature of 15° C. = 59° F.

Specific weight is generally expressed in numbers which denote how many times the weight of an equal bulk of water is contained in the weight of the substance in question. If we say that mercury has a specific gravity or density of 13.6, or that alcohol has a specific gravity of 0.79, we mean that equal volumes of water, mercury, and alcohol represent weights in the proportion of 1, 13.6, and 0.79, or 100, 1360, and 79.

The standard or unit chosen for comparing the specific gravity of gases is either atmospheric air or hydrogen.

In order to obtain the specific gravity of any liquid, it is only necessary to weigh equal volumes of water and the liquid to be examined, and then to divide the weight of the liquid by the weight of the water.

A second method by which the specific gravity of liquids may be determined is by means of the instruments known as hydrometers, or, if made for some special purposes, as alcoholometers, urinometers, alkalimeters, lactometers, etc.

Hydrometers are instruments generally made of glass tubes, having a weight at the lower end to maintain them in an upright position in the fluid to be tested as to specific gravity, and a stem above, bearing a scale. The principle upon which their construction depends is the fact that a solid substance when placed in a liquid heavier than itself displaces a volume of this liquid equal to the whole weight of the displacing substance. The hydrometer will consequently sink lower in liquids of lower specific gravity than in heavier ones, as the instrument has to displace a larger bulk of liquid in the lighter than in the heavier liquid in order to displace its own weight.

Weight of gases. We have so far considered the gravity of solids and liquids only, and the next question will be: Do gases also possess weight—are they also attracted by the earth? The fact that a gas, when generated or liberated, expands in every direction, might indicate that the molecules of a gas have no weight, are not attracted by the earth. A few simple experiments will, however, show that gases, like all other substances, have weight. Thus a flask from which the atmospheric air has been removed will weigh less than the same flask when filled with atmospheric air or any other gas.

Barometer. A second method by which may be demonstrated the fact that atmospheric air possesses weight, is by means of the barometer. The atmosphere is that ocean of gas which encircles the earth with a layer some 50 or 100 miles in thickness, exerting a considerable pressure upon all substances by its weight. The instruments used for measuring that pressure are known as barometers, and the most common form of these is the mercury barometer. It may be constructed by filling with mercury a glass tube closed at one end (and about three feet long) and then inverting it in a vessel containing mercury, when it will be found that the mercury no longer fills the tube to the top, but only to a height of about 30 inches, leaving a vacuum above. The column of mercury is maintained at this height by the pressure of the atmosphere upon the surface of the mercury in the vessel; a column of mercury about 30 inches high must consequently exert a pressure equal to the pressure of a column of the atmosphere of the same diameter as that of the mercury column.

As the weight of a column of mercury, having a base of one square inch and a height of about 30 inches, is equal to about 15 pounds, a column of atmosphere having also a base of one square inch must also weigh 15 pounds. In other words, the atmospheric pressure is equal to about 15 pounds to the square inch, or about one ton to the square foot. This enormous pressure is borne without inconvenience by the animal frame in consequence of the perfect uniformity of the pressure in every direction.

lbs to
inch

A barometer may be constructed of other liquids than mercury, but as the height of the column must always bear an inverse proportion to the density of the liquid used, the length of the tube required must be greater for lighter liquids. As water is 13.6 times lighter than mercury, the height of a water column to balance the atmospheric pressure is 13.6 times 30 inches, or about 34 feet, which would therefore be the height of the column of water required.

Changes in the atmospheric pressure. The height of the mercury column in a barometer is not the same at all times, but varies within certain limits. These variations are due to a number of causes disturbing the density of the atmosphere, and are chiefly atmospheric currents, temperature, and the amount of moisture contained in the atmosphere.

As the height and with it the density of the atmosphere diminishes gradually from the level of the sea upward, the height of the mercury column will be lower in localities situated at an elevation. This diminution of pressure is so constant that the barometer is used for estimating elevations.

Influence of pressure on state of aggregation. We have seen that the volume of a substance, and, more especially, of a gas, depends upon pressure and temperature, an increase of pressure or decrease of temperature causing the volume to become smaller. We learned also that liquids may be converted into gases, and that this conversion takes place at a certain fixed temperature called the boiling-point. This point, however, changes with the pressure. An increased pressure will raise, a decreased pressure will lower, the boiling-point.

Thus water boils at the normal pressure of one atmosphere at 100° C. (212° F.), but it will boil at a lower temperature on mountains in consequence of the diminished atmospheric pressure. If the pressure be increased, as, for instance, in steam-boilers, the boiling-point will be raised. Thus the boiling-point of water under a pressure of two atmospheres is at 122° C. (251° F.), of five atmospheres at 153° C. (307° F.), of ten atmospheres at 180° C. (356° F.)

QUESTIONS.—21. What is gravitation? 22. Mention some phenomena caused by gravitation? 23. Give a definition of weight. 24. What is specific weight? 25. Name the substances adopted as standards for the determination of specific gravities of solids, liquids, and gases. 36. What is the use made of hydrometers, and on what principle is their construction based? 27. Explain construction and use of the mercury barometer. 28. Mention some of the causes which have an influence upon the height of the mercury column in the barometer. 29. What is the atmospheric pressure upon a surface of five square feet? 30. State the relation between boiling-point, temperature, and pressure.

4. POROSITY.

Nature of porosity. We have seen that the molecules of any substance are not in absolute contact, but that there are spaces between them which we call intermolecular spaces; the property of matter to have spaces between the particles composing it is known as *porosity.*

In the case of solids, these spaces or pores are sometimes of considerable size, visible even to the naked eye, as, for instance, in charcoal, whilst in most cases they cannot be discovered, even by the microscope. That even apparently very dense substances are porous, can be demonstrated by the fact that liquids may be pressed through metallic disks of considerable thickness, that gases may be caused to pass through plates of metal or stone; that solids dissolve in liquids without showing a corresponding increase in volume of the solution thus obtained, and, finally, also by the fact that substances suffer expansion or contraction in consequence of increased or diminished heat, or in consequence of mechanical pressure.

Surface. In every-day life the expression "surface" refers to that part of a substance which is open to our senses, visible and measurable; but from a more scientific point of view, we have also to take into consideration those surfaces which, in consequence of porosity, extend to the interior of matter and are invisible to our eyes and absolutely immeasurable by instruments.

Surface-action. Attraction acts differently under different conditions, and, accordingly, we assign different names to it. We call it cohesion when it acts between molecules, gravitation when acting between masses, and surface-action or surface-attraction when the attraction is exerted either by the visible surface or by that surface which pervades the whole interior of matter. The phenomena caused by this surface-action are extremely manifold, and some are of sufficient interest to be taken into consideration.

Adhesion. Most solid substances, when immersed in water, alcohol, or many other liquids, become moist; immersed in mercury, they remain dry. We explain this fact by saying that the surfaces of most solid substances exert an attraction for the particles of such liquids as water and alcohol to such an extent that these particles adhere to the surface of the solids. Such an attraction, however, does not manifest itself for the particles of mercury. This form of surface-attraction by which liquids are caused to adhere to solids is called *adhesion.*

This adhesion may be noticed also between two plates having plane surfaces. A drop of water pressed between these plates will cause them to adhere to each other. The application and use of glue and mucilage, our methods of writing and painting, the welding together of pieces of metal, etc., depend on this kind of surface-action.

Capillary attraction. Whilst it is the general rule that liquids in vessels present a horizontal surface, this rule does not hold good near the sides of the vessel. When the liquids wet the vessel, as in the case of water in a glass vessel, the surface is somewhat concave in consequence of the attraction of the glass surface for the particles of water; on the contrary, when the liquids do not wet the vessel, as in the case of mercury in a glass vessel, the surface is somewhat convex. The smaller the diameter of the vessel holding the liquids, the more concave or convex will the surface be. If a narrow tube is placed in a liquid, this surface-action will be more striking, and it will be found that a liquid wetting the tube will not only have a completely concave surface, but the level of the liquid stands perceptibly higher in the tube than the level of the liquid outside. Substances not wetting the tube will show the reverse action, namely, the surface inside of the tube will be convex, and will be below the level of the liquid outside.

The attraction of the surface of tubes for liquids, manifesting itself in the concave shape of the surface and in the elevation of the liquid near the tube, is known as *capillary attraction.* Capillary elevations and depressions depend upon the diameter of the tube, temperature, and the nature of the liquid. The narrower the tube, the higher the elevation or the lower the depression; both are diminished by increased temperature. Capillary elevations and depressions, all other circumstances being equal, are inversely proportional to the diameters of the tubes.

Defining the phenomena of capillary attraction more scientifically, we may say that the adhesive force of glass, wood, etc., for water and most other liquids exceeds the cohesive force acting between the molecules of these liquids, while in mercury the cohesive force predominates over the adhesive.

Surface-attraction of solids for gases. Any dry solid substance, carefully weighed, will, after having been exposed to a higher temperature, show a decrease in weight whilst yet warm. Upon cooling, the original weight will be restored. This fact cannot be explained otherwise than that some substance or substances must have been expelled by heat, and that this substance or these substances are reabsorbed on cooling.

This is actually the case, and the substances expelled and reabsorbed are the gaseous constituents of the atmospheric air, chiefly the aqueous vapor.

Every solid substance upon our earth condenses upon its surface more or less of the gaseous constituents of the atmosphere. This condensation takes place upon the outer as well as upon the inner surface. The amount of gas absorbed depends upon the nature of the gas as well as upon the nature of the absorbing solid. Some of the so-called porous substances, such as charcoal, generally condense or absorb larger quantities than solids of a more dense and compact structure. Heat, as stated above, counteracts this absorbing power.

Surface-attraction of solids for liquids or for solids held in solution. When a mixture of different liquids, or a mixture of different solids dissolved in a liquid, is brought in contact with or filtered through a porous solid substance, such as charcoal or bone-black, it will be found that the surface of the solid substance retains a certain amount of the liquids or of the solids held in solution, and that it retains more of one kind than of another.

It is this peculiarity of surface-attraction which is made use of in purifying drinking-water by allowing it to pass through charcoal. Bone-black is similarly used for decolorizing sugar-syrup and other liquids.

Absorbing power of liquids. In a similar manner as in the case of solids, liquids also exert an attraction for gases. When a gas is condensed within the pores or upon the surface of a solid, or when it is taken up and condensed by a liquid, we call the process *absorption.* This absorbing power of different liquids for different gases varies greatly; it is facilitated by low temperature and high pressure, and counteracted by high temperature and removal of pressure. Thus: One volume of water absorbs at ordinary temperature and pressure about 0.03 volume of oxygen, 1 volume of carbon dioxide, 30 volumes of sulphur dioxide, and 800 volumes of ammonia.

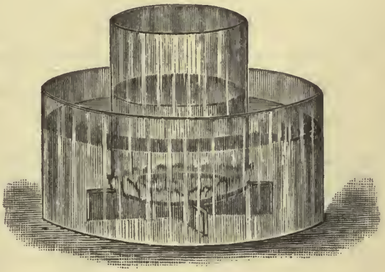
Diffusion. When a cylindrical glass vessel has been partially filled with water, and alcohol, which is specifically lighter than water, is poured upon it, care being taken to prevent a mixing of the two liquids, so as to form two distinct layers, it will be found that after a certain lapse of time the two liquids have mixed with each other, particles of water having entered the alcohol and particles of alcohol the water, until a uniform mixture of the two liquids has taken place. Upon repeating the experiment with a layer of water over a column of solution of common salt, it will again be found that the two liquids gradually enter one into the other until a uniform salt solution has been formed.

In a similar manner, two or more gases introduced into a vessel or a room will readily mix with each other. This gradual passage of one liquid into another, of a dissolved substance into another liquid, or of one gas into another gas, is called *diffusion.*

Osmose. Dialysis. This diffusion takes place also when two liquids are separated by a porous diaphragm, such as bladder or parchment paper, and it is then called *osmose* or *dialysis.*

The apparatus used for dialysis is called a *dialyzer* (Fig. 4), and consists usually of a glass cylinder, open at one end and closed at the other by the membrane to be used as the separating medium. This vessel is placed into another, and the two liquids are introduced into the two vessels. If the inner vessel be filled with a salt solution and the outer one with pure water, it will be found that part of the salt solution passes through the membrane into the water, whilst at the same time water passes over to the salt solution.

FIG. 4.



Dialyzer.

On subjecting different substances to this process of dialysis, it has been found that some substances pass through the membrane with much greater facility or in larger quantities than others, and that some do not pass through at all. As a general rule, crystallizable substances pass through more freely than amorphous substances. Those substances which do not pass through membranes in the process of dialysis are known as *colloids,* those which diffuse rapidly *crystalloids.*

Capillary attraction, or, more generally speaking, surface-attraction, is undoubtedly to some extent the cause of the phenomena of osmose, the surface of the diaphragm exercising an attraction upon the liquids.

Diffusion of gases. A diffusion similar to that of liquids takes place also when two different gases are separated from each other by some porous substance, such as burned clay, gypsum, and others.

It has been found that specifically lighter gases diffuse with greater rapidity than the heavier ones. The quantities of two different gases which diffuse into one another in a given time are, as a general rule, inversely as the square roots of their specific gravities. Oxygen is sixteen times as heavy as hydrogen; when the two gases diffuse, it will be found that four times as much hydrogen has penetrated into the oxygen as of the latter gas into the hydrogen. This regularity in the diffusion of gases is expressed in the *Law of Graham*, thus: The velocity of the diffusion of any gas is inversely proportional to the square root of its density.

Indestructibility. All matter is indestructible—*i. e.*, cannot possibly be destroyed by any means whatever, and this property is known as *indestructibility*. Form, shape, appearance, properties, etc., of matter may be changed in many different ways, but the matter itself can never be annihilated. Apparently, matter often disappears, as, for instance, when water evaporates or oil burns; but these apparent destructions indicate simply a change in the form of matter; in both cases gases are formed, which become invisible constituents of the atmospheric air, and can, therefore, not be seen for the time being, but may be recondensed or rendered visible in various ways.

Not only is matter indestructible, energy also partakes of this property. Energy may be converted from one form into some other form. Motion may be converted into heat, and heat into motion, or this motion into electrical energy and chemical energy. In fact, all the different forms of energy are convertible one into the other without loss. This fact is spoken of as the *Law of the conservation of energy.*

To repeat: The total quantity of matter in the universe is constant, and the same is true of energy.

QUESTIONS.—31. What is porosity? 32. What two meanings may be assigned to the word surface? 33. Mention some phenomena caused by surface-action. 34. Explain the term adhesion. 35. Under what circumstances can capillary attraction be noticed, and how does it manifest itself? 36. Give an explanation of the word absorption, and mention some instances of the absorption of gases by solids or liquids. 37. What do we understand by diffusion of gases or liquids? 38. Define the word osmose. 39. Which substances are most apt to dialyze, and which have no such tendency? 40. What is meant by saying that matter and energy are indestructible?

II.

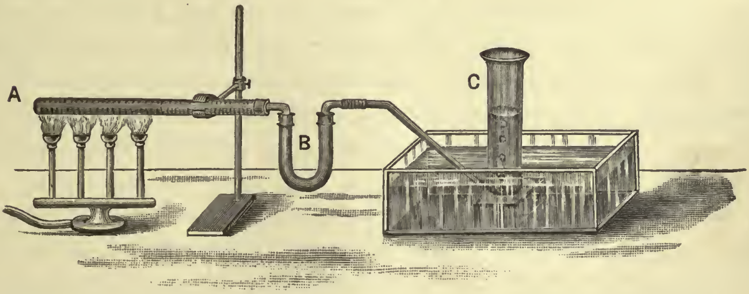
PRINCIPLES OF CHEMISTRY.

RESULTS OF THE ATTRACTION BETWEEN ATOMS.

5. CHEMICAL DIVISIBILITY.

Decomposition by heat. The results of the action of heat upon matter have been stated to be: Increased velocity of the motion of molecules, increase in volume of the substance heated, and in many cases a conversion of solids into liquids and of these into gases. Besides these results there frequently may be noticed another, now to be mentioned.

Fig. 5.



Decomposition of mercuric oxide in A; collection of mercury in B, and of oxygen in C.

To illustrate this action of heat, we will select the red oxide of mercury, a solid substance which is insoluble in water, almost tasteless, and of a brick-red color. When this oxide of mercury is placed in a glass tube and heated, it will be found to disappear gradually, and we might assume that it has been converted into a gas from which, upon cooling, the red oxide of mercury would be re-obtained. If the apparatus for heating the oxide of mercury be so constructed that the escaping gases may be collected and cooled, we shall not find the red oxide in our receiver, but in its place a colorless gas, whilst at the same time globules of metallic mercury will be found deposited in the cooler parts of the apparatus (Fig. 5).

The action of heat consequently has in this case produced an effect entirely different from the effects spoken of heretofore. There is no doubt that the first action of the heat upon the oxide of mercury is an increased velocity of the motion of its molecules and simultaneously an increase of its volume, but afterward a decomposition of the oxide takes place, and two substances are liberated, each different from the oxide.

One of these substances is a silvery-white, heavy, liquid metal, the mercury; the other substance is a colorless, odorless gas, which supports combustion much more freely than does atmospheric air, and is known as oxygen.

Elements. We have thus succeeded in proving that red oxide of mercury may be converted or decomposed by the mere action of heat into mercury and oxygen. It is but natural to inquire whether it would be possible further to subdivide the mercury or the oxygen into two or more new substances of different properties. To this question, which has been experimentally propounded to Nature over and over again, we have but one answer, viz.: Oxygen and mercury are substances incapable of decomposition by any method or means as yet known to us. They resist the powerful influences of electricity and heat, even when raised to the highest attainable degrees of intensity, and they issue unchanged from every variety of reaction hitherto devised with the view of resolving them into simpler forms of matter.

Therefore we are justified in regarding oxygen and mercury as non-decomposable or simple substances, in contradistinction to compound or decomposable substances, such as the red oxide of mercury.

All substances which cannot by any known means be resolved into simpler forms of matter, are called *elements;* all substances which may, by one process or another, be subdivided or decomposed in such a manner that new substances with new properties are formed, are called *compound substances* or *compounds.*

While the number of known compounds exceeds many thousands, the number of elements is comparatively small, but sixty-seven of these simple substances being known to exist on our earth. And yet this small number of elements, by combining with each other in many different proportions, form all that boundless variety of matter which we see in nature.

Chemical affinity. There must be some cause which enables or even forces the different elements to unite with each other so as to form compound bodies. There must be, for instance, a cause which enables oxygen and mercury to combine and form a red powder.

This cause is to be found in the existence of another form of the general attraction which causes the smallest particles of different elements to unite to form new substances with new properties. This kind of attractive power is called *chemical force* or *chemical affinity*, and bodies possessing this capacity of uniting with each other are said to have an affinity for each other.

There is a great difference between chemical attraction and the various forms of attraction spoken of heretofore. Cohesion simply holds together the molecules of the same substance, adhesion acts chiefly between the molecules of solid and liquid substances, gravitation acts between masses. But all these forces do not change the nature, the external and internal properties of matter; this is done when chemical force or affinity is operating, when a chemical change takes place.

For instance: In a piece of yellow sulphur the molecules are held together by cohesion, and we can counteract this cohesion by mechanical subdivision, reducing the sulphur to a fine powder; or by the application of heat we can further subdivide the sulphur, melt, and finally volatize it; or we can throw a piece of sulphur into the air, when it will fall back upon the earth in consequence of gravitation; or we can dip it into water, when it becomes moist in consequence of surface-action. Yet in all these cases sulphur remains sulphur.

It is entirely different when sulphur enters into chemical combination exerting chemical attraction, for instance, when it burns; this means when it combines with the oxygen of the atmospheric air. In this case a new substance, a disagreeably smelling gas, a compound of oxygen and sulphur, is formed.

It is consequently a complete change in the properties of matter which follows the action of true chemical attraction; we might define affinity to be a force by which elements unite and new substances are generated.

Atoms. Molecules, as stated heretofore, are the smallest particles of matter which can exist. All matter consists of molecules, consequently the red oxide of mercury must also consist of molecules.

By heating the oxide of mercury, oxygen and mercury are obtained, each of which also must consist of molecules. As the oxide of mercury consists of molecules, and as these molecules are neither pure oxygen nor pure mercury, we must come to the conclusion that a molecule of the oxide of mercury is composed of a small particle of oxygen and a small particle of mercury. We consequently learn that a molecule of a compound substance is composed of yet smaller particles of elements, and *these smallest particles of elements capable of entering into combination are called atoms, while molecules are the smallest particles of matter which are capable of existing in a free state.*

Having now established the difference between atoms and molecules, we may give a better definition of elements and compounds by saying that an elementary substance is one in which the atoms composing its molecules are alike, while in a compound substance the molecules contain atoms of different kinds.

Chemistry is the science of affinity, and affinity is the attraction acting between atoms and causing them to unite and form molecules. As every chemical change is due to the motion of atoms, chemistry may also be defined as the *science of the motion of atoms taking place in consequence of chemical affinity.* Also, we may say that chemistry is that branch of science which treats of the composition of substances, the changes in their composition, and the laws governing such changes.

The scheme below may help to illustrate the relation of chemistry to some other branches of physical science:

GENERAL FORCE OF ATTRACTION.

acting between—

Heavenly bodies or masses.	*Surfaces.*	*Molecules.*	*Atoms.*

is termed:

Gravitation.	*Surface-action.* *Adhesion.* *Capillary attraction, etc.*	*Cohesion.*	*Chemical affinity.*

The phenomena caused by these respective actions are considered by:

Astronomy or Mechanics.	*Physics.*	*Physics.* *Crystallography.*	*Chemistry.*

Atomic weight. All matter possesses weight; this is true of a mass as well as any part of it, and must consequently be true of the atoms also and of the molecules of which matter consists. It is, of course, impossible to weigh a single atom or a single molecule, yet science has formed an opinion in regard to the relative weights of these minute particles. The experiment referred to above may be so conducted as to ascertain the weight of the products of decomposition (viz., the oxygen and the mercury) of a given, previously weighed quantity of oxide of mercury. In doing this, it will be found invariably that every 13.5 parts by weight of the oxide of mercury yield upon heating 12.5 parts by weight of mercury and 1 part of oxygen, that we have consequently in 13.5 pounds of oxide 12.5 pounds of mercury and 1 pound of oxygen.

If we assume that a molecule of the oxide is composed of one atom of mercury and one atom of oxygen, we are justified in saying that a mercury atom is 12.5 times heavier than an oxygen atom.

In a manner similar to this, the weights of the atoms of all different elements have been compared with each other, and the element having the lightest atom has been selected as the unit of comparison. The element having the lightest atom is hydrogen, and we say the atomic weight of hydrogen is 1, and compare with this weight the weights of all other elements. In doing this, we find that the atom of oxygen weighs sixteen times as much as the atom of hydrogen, and we consequently say the atomic weight of oxygen is 16.

H = 1
O = 16

We have learned before, from the decomposition of the red oxide of mercury, that the mercury atom is 12.5 times as heavy as that of oxygen. As the atomic weight of this element is 16, the atomic weight of mercury must be 12.5 times 16, or 200.

Whilst atomic weight is the weight of the atom of any element as compared to the weight of an atom of hydrogen, *molecular weight* is the combined weight of the atoms forming the molecule. Thus the molecular weight of oxide of mercury is $200 + 16 = 216$.

Chemical symbols. For reasons to be better understood hereafter, chemists designate each element by a symbol, and the first or first two letters of the Latin name of the element have generally been selected. Thus, the symbol of hydrogen is H, of oxygen O, of mercury Hg, (from hydrargyrum), of sulphur S, etc. These symbols designate, moreover, not only the elements, but one atom of these elements. For instance: O not only signifies oxygen, but one atom or 16 parts by weight of oxygen; and Hg, one atom or 200 parts by weight of mercury.

Chemical formulas. In a similar manner as atoms of elements are represented by symbols, the molecules of a compound substance are designated, and such a representation of a compound substance by symbols is called its formula. Thus, HgO is the formula of the red oxide of mercury, and it tells at once that it is a substance composed of one atom or 200 parts by weight of mercury, and one atom or 16 parts by weight of oxygen.

In the molecule of a compound body there must be at least two atoms, each one of a different element, but there may be in a molecule of a compound more than two atoms belonging to two or more elements.

For instance: The composition of water is H_2O; this means, a molecule of water contains 2 atoms of hydrogen and one atom of oxygen. When there is more than one atom of an element in a molecule, the number of these atoms is designated by placing the figure on the right of the symbol and a little below it, as in H_2O, whilst $2HO$ or $2OH$ would designate 2 molecules of a substance containing one atom of hydrogen and one atom of oxygen.

6. LAWS OF CHEMICAL COMBINATION.

Law of the constancy of composition. This law, also known as the law of definite proportions, was the first ever recognized in chemical science; it was discovered toward the close of the last century, and may be stated thus: *A definite compound always contains the same elements in the same proportion;* or, in other words, *All chemical compounds are definite in their nature and in their composition.*

To make this law perfectly understood, the difference between a mechanical mixture and a chemical compound must be pointed out. Two powders, for instance sugar and starch, may be mixed together very intimately in a mortar, so that it seems impossible for the eye to discover more than one body. But in looking at this powder with the aid of a microscope, the particles of sugar as well as those of starch may be easily distinguished. The mixture thus produced is a *mechanical mixture of molecule clusters.*

Questions.—41. How does heat act upon the red oxide of mercury? 42. State the difference between mechanical and chemical divisibility. 43. Define the terms element and compound. 44. How many elements and how many compound substances are known? 45. What is chemical affinity, and how does it differ from other forces? 46. What is an atom, and how does it differ from a molecule? 47. What is chemistry? 48. Give a definition of atomic weight and of molecular weight. 49. The atom of which element has been selected as the unit for comparison of atomic weights? 50. Give an explanation of chemical symbols and formulas.

It is somewhat different when two substances, for instance two metals, are fused together, or when two gases or two liquids (oxygen and nitrogen, water and alcohol) are mixed together, or when finally a solid is dissolved in a liquid (sugar in water). In these instances no separate particles can be discovered even by the microscope. The mixtures thus produced are *mixtures of molecules*. Such mixtures always exhibit properties intermediate between those of their constituents and in regular gradation according to the quantity of each one present. The proportions in which substances may be mixed are variable.

In a true chemical compound the proportions of the constituent elements admit of no variation whatever; it is not formed by the mixing of molecules, but by the *combination of atoms into molecules;* the properties of a compound thus formed usually differ very widely from those of the combining elements.

Powdered iron and powdered sulphur may be mixed together in many different proportions. If such a mixture be heated until the sulphur becomes liquid, the two elements, iron and sulphur, combine chemically, but they do so in one proportion only, 56 parts by weight of iron combining with 32 parts by weight of sulphur to form 88 parts of sulphide of iron. If the two substances had been mixed together in any other proportion than the one mentioned, and which corresponds to the atomic weights of both elements, the excess of one will be left undisturbed and uncombined.

Law of multiple proportions. If two elements, A and B, are capable of uniting in several proportions, the quantities of B which combine with a fixed quantity of A bear a simple ratio to each other. Thus A may combine with B, or A with 2 B, or A with 3 B, etc.

This law was discovered at the beginning of the present century, when it was found that the ratio of carbon to hydrogen in olefiant gas, C_2H_4, is as 6 to 1, in marsh gas, CH_4, as 6 to 2, and that the ratio of carbon to oxygen in carbon monoxide, CO, is as 6 to 8, in carbon dioxide, CO_2, as 6 to 16.

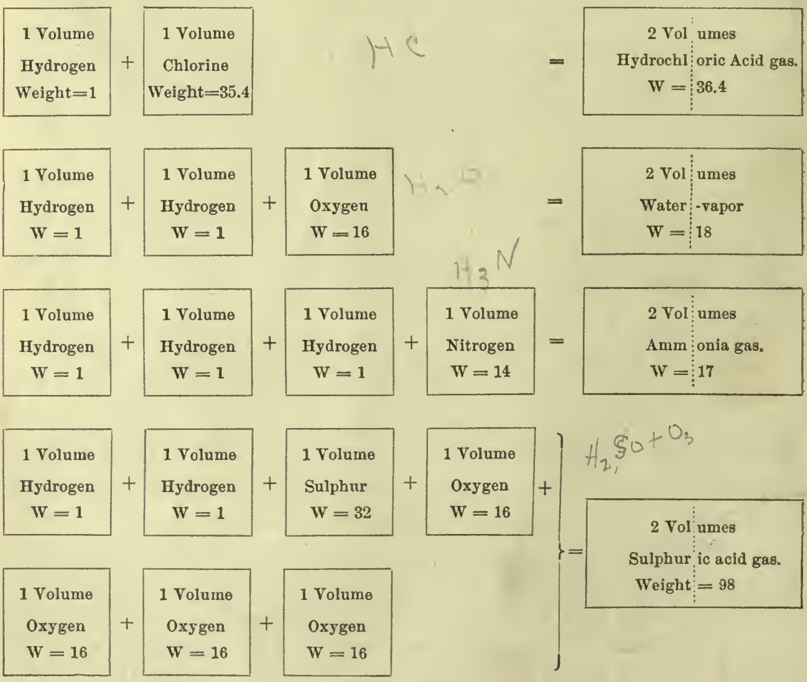
These and similar instances led to the discovery of the law of multiple proportions, and it was this law which led *Dalton,* in 1804, to the adoption of the atomic theory. In thinking and reasoning about this law, he could find no other explanation than that there must be small particles of definite weight which combine with each other, and to these small particles he gave the name atoms.

As a very good example illustrating the law of multiple proportions may be mentioned the five compounds formed by the elements nitrogen and oxygen, which compounds have the composition N_2O, N_2O_2, N_2O_3, N_2O_4, and N_2O_5, respectively. In these compounds we find 16, 2×16, 3×16, 4×16, and 5×16 parts by weight of oxygen in combination with 28 parts by weight of nitrogen.

The law of chemical combination by volume, or the *Law of Gay-Lussac,* may be stated as follows: *When two or more gaseous constituents combine chemically to form a gaseous compound, the volumes of the individual constituents bear a simple relation to the volume of the product.* The law may be divided into two laws, thus: 1. Gases combine by volume in a simple ratio. 2. The resulting volume of the compound, when in the form of a gas, bears a simple ratio to the volumes of the constituents. For instance: 1 volume of hydrogen combines with 1 volume of chlorine, forming 2 volumes of hydrochloric acid gas; 2 volumes of hydrogen combine with 1 volume of oxygen, forming 2 volumes of water-vapor; 3 volumes of hydrogen combine with 1 volume of nitrogen, forming 2 volumes of ammonia.

If the different combining volumes of the gases mentioned are weighed, it will be found that there exists a simple relation between these volumes and the atomic or molecular weights of the elements.

For instance: Equal volumes of hydrogen and chlorine combine, and the weights of these volumes are as 1 : 35.4, which numbers represent also the atomic weights of the two elements. Two volumes of hydrogen combine with one volume of oxygen, and the weights of the volumes are as 1 : 8 or 2 : 16, the latter being the atomic weight of oxygen.



The above diagram shows the simple relation which exists between combining volumes, and atomic and molecular weights; that such a relation exists is not surprising, if we remember the law of Avogadro, which has been before stated, and which says that all gases under equal conditions contain the same number of molecules.

The weighing of equal volumes of gases consequently is identical with the weighing of equal numbers of molecules. The molecular weight of a substance therefore can be found by weighing this substance in the gaseous state and comparing with it the weight of an equal volume of another gas, the molecular weight of which is known. The gas usually adopted for this comparison is hydrogen.

If, for instance, we weigh equal volumes of hydrogen, chlorine, oxygen, hydrochloric acid gas, and steam, we find weights in the proportion of 2, 70.8, 32, 36.4, and 18. These numbers express also the molecular weights of these substances; moreover, they show that atomic and molecular weights of *elements* are not identical, but that the latter weight is twice that of the atomic weight, or that the *molecules of elements consist of two atoms.*[1]

One litre of hydrogen at the freezing-point of water and under the ordinary pressure of 15 pounds to the square inch, weighs 0.0896 gramme. This weight of one litre of hydrogen is taken as the unit or standard of comparison for gases, and is called one *crith.* A litre of oxygen weighs 16 criths, one of chlorine 35.4 criths, one of steam 9 criths, etc.

Theory (Law) of equivalents. Valence, or Quantivalence. When one element replaces another element in a compound, the quantities of the two elements are said to be equivalent to each other, and according to the law of equivalents the replacement of elements one by another takes place always in definite proportions. Formerly it was believed that the atoms of all elements were equivalent one with another; accordingly, atomic weights were frequently designated as equivalent weights.

This view, however, is not correct, as it is found that one atom of one element frequently displaces two or more atoms of another element. This fact, as well as other considerations, has led to the assumption of the quantivalence of atoms. This property will be understood best by selecting for consideration a few compounds of different elements with hydrogen.

I.	II.	III.	IV.
HCl	H_2O	H_3N	H_4C
HBr	H_2S	H_3As	H_4Si
HI	H_2Se	H_3P	

---

[1] A few exceptions to this general rule will be mentioned in the proper places.

We see here that Cl, Br, and I combine with H in the proportion of atom for atom; O, S, Se combine with H in the proportion of 2 atoms of hydrogen for 1 atom of the other element; N, As, P combine with 3; C and Si with 4 atoms of hydrogen.

Moreover, it has been found that the compounds mentioned in column I. are the only ones which can be formed by the union of the elements Cl, Br, and I with H. They invariably combine in this proportion only. Other elements show a similar behavior. For instance, the metal sodium combines with chlorine or bromine in one proportion only, forming the compound NaCl or NaBr.

Looking at columns II., III., and IV., we see that the elements mentioned there combine with 2, 3, and 4 atoms of hydrogen, respectively. It is evident, therefore, that there must be some peculiarity in the power of attraction of different elements toward other elements, and to this property of the atoms of elements of holding in combination one, two, three, four, or more atoms of other elements the name *atomicity, quantivalence,* or simply *valence,* has been given.

According to this theory of the valence of atoms, we distinguish univalent, bivalent, trivalent, quadrivalent, quinquivalent, sexivalent, and septivalent elements. All elements which combine with hydrogen in the proportion of one atom to one atom are univalent, as, for instance, Cl, Br, I, F, and all elements which combine with these in but one proportion, that is, atom with atom, bear the same valence, or are also univalent, as, for instance, Na, K, Ag, etc.

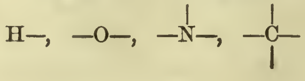
Those elements which combine with hydrogen or other univalent elements in the proportion of one atom to two atoms are bivalent, such as O, S, Se.

Trivalent and quadrivalent elements are those the atoms of which combine with 3 or 4 atoms of hydrogen, respectively. Figuratively speaking, we may say that the atoms of univalent elements have but one, those of bivalent elements two, of trivalent elements three, of quadrivalent elements four *bonds* or points of attraction, by means of which they may attach themselves to other atoms.

Elementary atoms are often named according to their valence: *monads, diads, triads, tetrads, pentads, hexads, and heptads.*

To indicate the valence of the elements frequently dots or numbers are placed above the chemical symbols, thus H^{i}, O^{ii}, N^{iii}, C^{iiii} or C^{iv}.

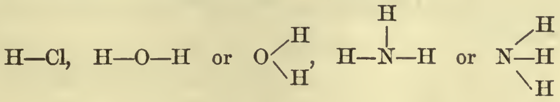
The bonds are often graphically represented by lines, thus:



$$\mathrm{H}-,\quad -\mathrm{O}-,\quad -\overset{|}{\mathrm{N}}-,\quad -\underset{|}{\overset{|}{\mathrm{C}}}-$$

It is needless to say that such representations are merely symbolical, and express the view that atoms have a definite power to combine with others.

When atoms combine with one another the bonds are said to be satisfied, and it is graphically expressed thus:



$H{-}Cl$, $H{-}O{-}H$ or $O\begin{smallmatrix}/H\\ \backslash H\end{smallmatrix}$, $H{-}\overset{H}{\overset{|}{N}}{-}H$ or $N\begin{smallmatrix}/H\\ -H\\ \backslash H\end{smallmatrix}$

Whilst the valence of some elements is invariably the same under all circumstances, other elements show a different valence (this means a different combining power for other atoms) under different conditions. For instance: Phosphorus combines both with 3 and 5 atoms of chlorine, forming the compounds PCl_3 and PCl_5. As chlorine is a univalent element, we have to assume that phosphorus has in one case 3, in another case 5 points of attraction. Many similar instances are known, and will be spoken of later.

The only explanation which we can furnish in regard to the variability of the valence of atoms is the assumption that sometimes one or more of the bonds of an atom unite with other bonds of the same atom. If, for instance, in the quinquivalent phosphorus atom two bonds unite with one another a trivalent atom will remain.

It is noticed invariably that the valence of atoms increases or diminishes by two, which could not be otherwise, if the explanation given be correct. Thus chlorine, the valence of which generally is I., may also have a valence equal to III., V., or VII., while sulphur shows a valence either of II., IV., or VI. Atoms whose valence is even, as in case of sulphur, are called *artiads;* those whose valence is expressed in uneven numbers, as chlorine and phosphorus, are called *perissads.*

While it is now being assumed that most of the elements possess more than one valence, in consequence of the assumed power of bonds in the same atom to saturate one another, in this book will be mentioned chiefly that valence which the element seems to possess predominantly.

The doctrine of the valence of atoms has modified our views of the equivalence of atoms. We now say that all atoms of a like valence are equivalent to each other. The atoms of each univalent element are equivalent to each other, and so of the atoms of any other valence, but two atoms of a univalent element are equivalent to one atom of a bivalent element, or two atoms of a bivalent element to one atom of a quadrivalent element, etc.

After having explained this valence of atoms, it now may be better understood why the atoms in an element do not exist in a free or uncombined state, but combine with each other to form molecules. Atoms having the tendency of combining with, or attaching themselves to other atoms, are bound to exert that attraction, and if they are not combined with atoms of other elements, they combine with each other. For instance: Oxygen gas is not a mass of oxygen atoms, but of oxygen molecules, each molecule being formed by the union of two atoms.

7. DETERMINATION OF ATOMIC AND MOLECULAR WEIGHTS.[1]

Determination of atomic weights by chemical decomposition. The great difficulties originally encountered in the determination of atomic weights cannot well be described here. Consideration will be given alone to the three principal methods at present in use. These methods depend either on chemical action or on physical properties.

One of the chemical methods used for the determination of atomic weights has been stated before in describing the decomposition of the red oxide of mercury by heat. The principle of this method is the determination of the proportions by weight in which the element, the atomic weight of which is unknown, combines with an element the atomic weight of which is known. For instance: If in decomposing a substance we find it to contain in 72 parts by weight, 16 parts by weight of oxygen and 56 parts by weight of another element, we have a right to assume the atomic weight of this second element to be 56, provided, however, that the compound is actually formed by the union of one atom of oxygen and one atom of the other element. These 56 parts by weight might, however, represent 2 or 3 or more

QUESTIONS.—51. State the law of the constancy of composition. 52. What is the difference between a mixture and a chemical compound? 53. Mention some instances of the production of molecular mixtures. 54. State the law of multiple proportions. 55. What considerations led Dalton to the adoption of the atomic theory? 56. What regularity regarding volume is noticed when gases combine chemically? 57. To what was the term equivalent quantities applied formerly, and what is to be understood by it to-day? 58. Explain the term quantivalence or atomicity. 59. Mention some univalent, bivalent, trivalent, and quadrivalent elements. 60. Suppose a certain volume of hydrogen to weigh 20 grains, how much will an equal volume of oxygen and how much will an equal volume of hydrochloric acid gas weigh, provided pressure and temperature be the same?

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[1] The consideration of Chapter 7 should be postponed until the student has become familiar with chemical phenomena generally.

atoms. If 56 represented 2 atoms, the atomic weight would be but 28; if 4 atoms, 14.

As this mode of determination gives no clue to the number of atoms present in the molecule, the results obtained are liable to be incorrect. In fact, the atomic weights of a number of elements had originally been determined incorrectly by using the above or similar methods, and many of these old atomic weights had to be changed (generally doubled) in order to obtain the correct numbers.

Thus, in examining water, it was found that it contained 8 parts by weight of oxygen to 1 part of hydrogen, and the conclusion was drawn that the atomic weight of oxygen was 8, and that the molecule of water was formed by the union of one atom of hydrogen and one atom of oxygen. It will be demonstrated below why we assume to-day that the atomic weight of oxygen is 16, and that the molecule of water is composed of 2 atoms of hydrogen and 1 of oxygen.

Another chemical method of determining atomic weights is the replacement of hydrogen atoms in a known substance by the element the atomic weight of which is to be determined. For instance: Hydrochloric acid is composed of one atom of chlorine weighing 35.4, and one atom of hydrogen weighing 1, the molecular weight of hydrochloric acid being 36.4. If in this acid the hydrogen be replaced by some other element, for instance by sodium, we are enabled to determine the atomic weight of sodium by weighing its quantity and that of the liberated hydrogen. Suppose that by the action of 36.4 grammes of hydrochloric acid on sodium, 1 gramme of hydrogen was replaced by 23 grammes of sodium. In that case we would say that the atomic weight of sodium is equal to 23.

The difficulty which was alluded to above exists also in this mode of determination of atomic weights, viz., not knowing whether it was actually one atom of sodium that replaced the one part of hydrogen, a doubt is left as to whether or not the determination is correct.

Determination of atomic weights by means of specific weights of gases or vapors. It has been stated before that equal volumes of gases contain, under like conditions, the same number of molecules (no matter how few or many the atoms within the molecules may be), and that the molecules of elements contain (in most cases) two atoms. These facts give in themselves the necessary data for the determination of atomic weights.

For instance: If a certain volume of hydrogen is found to weigh 2 grammes, and an equal volume of some other gaseous element is found to weigh 71 grammes, then the atomic weight of the latter element must be 35.5, because 2 and 71 represent the relative weights of the molecules of the two elements. Each molecule being composed of 2 atoms, these molecular weights have to be divided by 2 in order to find the atomic weights, which are, consequently, 1 and 35.5 respectively.

In comparing by this method oxygen with hydrogen, it is found that equal volumes of these gases weigh 32 and 2 respectively, that the atomic weight of oxygen is consequently 16, and not 8, as determined by chemical methods.

This mode of determining atomic weights may be applied to all elements which are gases or which may without decomposition be converted into gas. There are, however, elements which cannot be volatilized, and in this case it becomes necessary to determine the specific gravity of some gaseous compound of the element. The element carbon itself has never been volatilized, but we know many of its volatile compounds, and these may be used in the determination of its atomic weight.

Determination of atomic weights by specific heat. Specific heat has been stated to be the quantity of heat required to raise the temperature of a given weight of any substance a given number of degrees, as compared with the quantity of heat required to raise the temperature of the same weight of water the same number of degrees.

In comparing atomic weights with the numbers expressing the specific heats, it is found that the higher the atomic weight the lower the specific heat, and the lower the atomic weight the higher the specific heat. This simple relation may be thus expressed: Atomic weights are inversely proportional to the specific heats; or the product of the atomic weight multiplied by the specific heat is a constant quantity for the elements examined.

Elements.	*Specific heats.* (Water = 1.)	*Atomic weights.*	*Product of specific heat* × *atomic weight.*
Lithium,	0 9408	7	6.59
Sodium,	0.2934	23	6.75
Sulphur,	0 2026	32	6 48
Zinc,	0 0956	65	6.22
Bromine (solid),	0.0843	80	6 75
Silver,	0.0570	108	6.16
Bismuth,	0.0308	209	6 44

An examination of this table will show this relation between atomic weight and specific heat, and also that the product of atomic weight multiplied by specific heat is equal to about 6.5. The variations noticed in this constant quantity of about 6.5 may be due to errors made in the determinations of the specific heats, and subsequent determinations may cause a more absolute agreement.

However, the agreement is sufficiently close to justify the deduction of a law which says: *The atoms of all elements have exactly the same capacity for heat.* This law was first recognized by Dulong and Petit in 1819, and is simply a generalization of the facts stated.

To show more clearly what is meant by saying that all atoms have the same capacity for heat, we will select three elements to illustrate this law.

If we take of lithium 7 grammes, of sulphur 32 grammes, of silver 108 grammes, we have of course in these quantities equal numbers of atoms, because 7, 32, and 108 represent the atomic weights of these elements. If we expose these stated quantities of the three elements to the same action of heat, we shall find that the temperature increases equally for all three substances—that is to say, the same heat will be required to raise 7 grammes of lithium 1°, which is necessary to raise either 32 grammes of sulphur or 108 grammes of silver 1°.

The quantity of heat necessary to raise the atom of any element a certain number of degrees is, consequently, the same. As heat is the consequence of motion, the result of the facts stated may also be expressed by saying: It requires the same energy to cause different atoms to vibrate with such a velocity as to acquire the same temperature, no matter whether these atoms be light or heavy.

It is evident that these facts give us another means of determining atomic weights, by simply dividing 6.5 by the specific heat of the element. The specific heat of sulphur, for instance, has been found to be 0.2026. 6.5 divided by this number is 31.6, or nearly 32. Originally the atomic weight of sulphur had been determined by chemical methods to be 16, but its specific heat, as well as other properties, has shown this number to be but one-half of the weight, 32, now adopted.

It may be mentioned that elements possess essentially the same specific heat whether they exist in a free state or are in combination; this fact will, in many cases, be of use in the determination of atomic weights.

Determination of molecular weights. From the statements made regarding the determination of atomic weights, it is evident that we may use a number of methods for determining molecular weights, these methods being to some extent analogous to the former.

Thus we have methods which are based entirely on chemical analysis or on chemical changes generally. If, for instance, the analysis of a substance shows of calcium 40 per cent., of carbon 12 per cent., and of oxygen 48 per cent., we have a right to assume that the molecule is made up of 1 atom of calcium, 1 atom of carbon, and 3 atoms of oxygen, as the atomic weights of these elements are 40, 12, and 16 respectively. The molecular weight in this case is 100, and the composition is expressed by the formula $CaCO_3$, but the molecular weight might be 200 and the correct formula $Ca_2C_2O_6$. There are actually substances which contain such multiples of atoms, as, for instance, the compounds C_2H_2 and C_6H_6, and as their percentage composition is identical, analytical methods are insufficient to indicate the number of atoms contained in these molecules.

The second method, based on Avogadro's law, is applicable to all substances which are or can be converted into gases or vapors without decomposition. Weighing equal volumes of hydrogen and of some other substance in the gaseous state gives at once the data for calculating the molecular weight. (See page 44.)

A third method, that of Raoult, is based upon the fact that the freezing-point of a liquid is lowered to the same extent by dissolving in it compounds in quantities proportional to their molecular weights. For example: Water begins to solidify at 32° F. (0° C.), but by dissolving in it say 4 per cent. of its weight of a salt (the molecular weight of which is known) the freezing-point is lowered, say 1° C. If, then, another salt (the molecular weight of which is not known) be dissolved in water, and it be found that to reduce the freezing-point 1° C. there must be dissolved a quantity equal to 7 per cent. of the weight of the water used—then are the molecular weights of the two salts to each other as is 4 to 7.

In regard to this method of Raoult it should be stated that it is applicable only to such substances as do not act chemically upon the

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QUESTIONS.—61. What are the three principal methods used for the determination of atomic weights? 62. Why are chemical means not always sufficient to determine atomic weights? 63. How can the specific gravity of elements in the gaseous state be used for the determination of atomic weight? 64. Describe a method of the determination of atomic weight by chemical means. 65. State one of the reasons why the atomic weight of oxygen has been changed from 8 to 16. 66. What relation exists between atomic weight and specific heat? 67. State the law of Dulong and Petit. 68. Suppose the specific heat of an element to be 0.1138, what will its atomic weight be? 69. Suppose the specific gravity of an elementary gas to be 14, what will its atomic weight be? 70. Suppose 216 grammes of an element replace 2 grammes of hydrogen in 73 grammes of HCl, what will the atomic weight of the element be?

solvent used, and that the ratio of the lowering of the freezing-point is not the same for all substances, but only for members of the same class of substances.

8. DECOMPOSITION OF COMPOUNDS. GROUPS OF COMPOUNDS.

Action of heat upon compounds. All phenomena taking place in nature are, without exception, due to motion. Chemistry considers the motion of atoms, without which no chemical change takes place. The causes for chemical changes are either physical actions (heat, light, electricity), or the decomposing influence of one substance upon another caused by the atoms rearranging themselves into new bodies, so as to better satisfy their affinities.

The decomposing action of heat upon compounds has been mentioned before in connection with the decomposition of red oxide of mercury into mercury and oxygen. Similarly to this process, many other compound substances are decomposed by heat either into elements, or, more frequently, into simpler forms of combination. This means that the molecule of a substance containing, for instance, 10 atoms, is split up into 2, 3, or more molecules, each one containing a portion of the 10 atoms.

For instance: A piece of marble, which is calcium carbonate, or $CaCO_3$, is decomposed by heat into calcium oxide, CaO, and carbon dioxide, CO_2.

That heat has such decomposing influence upon compounds is readily accounted for, if we bear in mind that increase in heat means increased molecular vibration, which most likely weakens the stability of the molecule, and diminishes the attractions of its component atoms. On the other hand, heat will in many cases facilitate chemical combination between two substances, because the increased molecular vibration brings the molecules closer within the sphere of each other's attraction, thereby facilitating chemical union. For instance: Mercury and oxygen do not act upon each other at ordinary temperature, but when heated to a temperature somewhat below the boiling-point of mercury, they combine slowly, forming oxide of mercury. This compound, however, as shown before, readily decomposes into mercury and oxygen when heated to a low red heat.

The quantity of heat required for decomposition differs widely according to the nature of the substance. Some substances can be produced only at a temperature below the freezing-point of water, a higher temperature causing their decomposition; other substances may be decomposed at temperatures between the freezing- and boiling-points; others again, and to these belong the majority of inorganic compounds, may be raised to red or white heat before decomposition sets in; and still another number of compounds have never yet been decomposed by heat. Theoretically, however, we assume that all compounds may be decomposed by heat, should it be possible to raise it to a sufficiently high degree.

Decomposition by electricity. Similarly to heat, also electricity decomposes many substances, provided they are in a liquid or gaseous state. These decompositions are usually accomplished by allowing an electric current to pass through the liquid, or electric sparks to pass through the gas. Thus hydrochloric acid, HCl, may be decomposed into hydrogen and chlorine; water, H_2O, into hydrogen and oxygen.

The act of decomposing a compound by electricity is known as *electrolysis*, and the substance thus decomposed is termed *electrolyte*. During the decomposition of substances by electrolysis one of the products of decomposition appears at the negative, the other at the positive pole of the battery. Thus, when water is decomposed, the hydrogen is evolved from the negative, the oxygen from the positive pole. Or, when salts are decomposed, the metal is deposited at the negative pole, and the acid or its decomposition products at the positive pole.

It was formerly believed that those elements which in electrolysis appear at the negative pole were charged with positive electricity, and were called *electro-positive elements*, while those appearing at the positive pole were charged with negative electricity and called *electro-negative elements*. According to this view the non-metals are electro-negative, while the metals are electro-positive.

There is a certain relation between electrical and chemical action, as the quantity of electricity which, for instance, sets free 35.4 grammes of chlorine, will also set free 80 grammes of bromine or 127 grammes of iodine. The figures 35.4, 80, and 127 represent the atomic weights of these elements.

Decomposition by light. Another cause of decomposition is, in many cases, the action of light. The art of photography is based upon this kind of decomposition. Many substances, easily affected by light, have to be kept in the dark to prevent them from being decomposed.

The phenomena of heat, light, and electricity resemble each other in so far as they are phenomena of motion. Heat is the consequence of the motion of material particles (molecules); light is the consequence of the vibratory motion of the hypothetical medium ether; probably the same is true of electricity.

These motions, in being transferred to atoms, have, as shown above, frequently the tendency of splitting up the molecules of compound substances.

Mutual action of substances upon each other. As a general rule, it may be said that no chemical action takes place between two substances both of which are in the solid state, because the molecules do not come in sufficiently close proximity to exchange their atoms. The free motion of the molecules in liquid or gaseous substances facilitates such a proximity, and consequently chemical action. It is often sufficient to have but one of the acting substances in the gaseous or liquid state, while the second one is a solid. By converting two solids into extremely fine powder and mixing them together thoroughly, chemical combination may follow, provided the affinity between them be sufficiently strong.

The action of substances upon each other may be represented by the following equations, in which the letters stand for elements or groups of elements :

1. $A + B = AB$ = direct combination.
2. $AB + C = AC + B$ = direct decomposition.
3. $AB + CD = AC + BD$ = double decomposition.

As instances illustrating the above, may be mentioned the following chemical reactions :

1. $$\underset{\text{Hydrogen.}}{H} + \underset{\text{Chlorine.}}{Cl} = \underset{\text{Hydrochloric acid.}}{HCl.}$$

The formula here given for the formation of hydrochloric acid is not entirely correct, because the action between hydrogen and chlorine does not take place between free atoms, but between the molecules of the two elements, each molecule containing two atoms. The more correct way of writing the formula would therefore be :

$$HH + ClCl = 2HCl.$$

Or

$$2H + 2Cl = 2HCl.$$

2. Hydrochloric acid and sodium form sodium chloride and hydrogen :

$$HCl + Na = NaCl + H.$$

The formula more correctly written would be :

$$2HCl + 2Na = 2NaCl + 2H.$$

3. $$\underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{HCl} + \underset{\substack{\text{Silver}\\ \text{Nitrate.}}}{AgNO_3} = \underset{\substack{\text{Silver}\\ \text{Chloride.}}}{AgCl} + \underset{\text{Nitric acid.}}{HNO_3.}$$

This form of decomposition, known as double decomposition or metathesis, is one of the common kinds of chemical changes met with in chemical operations.

All the decompositions mentioned above are caused by the affinity which the atoms of one substance have for atoms of another substance. For instance: The decomposition of hydrochloric acid by sodium may be explained by saying that sodium has a greater affinity for chlorine than for hydrogen, as the latter is expelled by the sodium.

No general rule can, however, be given for the intensity of affinity with which the atoms of different elements attract each other, because this attraction differs under different conditions. For instance: Water passed in the form of steam over red-hot iron is decomposed, iron oxide and free hydrogen being formed:

$$Fe + H_2O = FeO + 2H.$$

This decomposition would indicate that the attraction between iron and oxygen is greater than between hydrogen and oxygen. But in passing free hydrogen over heated iron oxide the reverse action takes place, water and free iron being formed:

$$FeO + 2H = Fe + H_2O.$$

This reaction would indicate that the affinity between oxygen and hydrogen is greater than between oxygen and iron.

As a general rule it may be stated that the quantity of a product formed by chemical action of two substances upon one another is influenced by the relative proportions of the reacting substances. In the above instance iron decomposes water when the iron is in large excess, while a liberal supply of hydrogen causes the reverse action. As a second instance may be mentioned the decomposition of sodium nitrate by sulphuric acid, with the formation of sodium acid sulphate and free nitric acid. On the other hand, sodium acid sulphate is decomposed by a large excess of nitric acid into sodium nitrate and free sulphuric acid.

A consideration of this *mass-action*, as it is now termed, has led to the establishment of the law, that *Chemical action is proportional to the active mass of each substance taking part in the change.*

recipitat

While the power of affinity possessed by atoms or compounds does not furnish us with data sufficient to predict all chemical changes, we may lay down a general rule which governs the decomposition of certain compounds and which may be stated thus: *When two* (or more) *substances are brought together in solution, which substances by any rearrangement of the atoms may form a product insoluble in the liquid present, this product will form and separate as a precipitate.*

As instances of this kind of decomposition may be mentioned the formation of all the hundreds of insoluble metallic salts, which are produced by the action of one salt solution upon another salt solution, the first solution containing a metal which with the acid of the second solution may form an insoluble compound, which is then invariably produced as a precipitate. For instance: Calcium carbonate, $CaCO_3$, is insoluble; if we bring together two solutions containing a soluble calcium salt and a soluble carbonate, such as calcium chloride, $CaCl_2$, and sodium carbonate, Na_2CO_3, calcium carbonate is precipitated.

A second general rule may be stated thus: *When two substances capable of forming a volatile product are brought together, the reaction generally takes place.* As instances may be mentioned the liberation of carbon dioxide from any carbonate by the action of an acid, and the liberation of ammonia gas from ammonium compounds by calcium hydroxide.

The nascent state. This expression is used of elements at the moment when their atoms leave molecules and have not yet had time to reënter into combination. When in this state the atoms have a much greater energy to combine than after having entered into a combination with other atoms of either the same kind (to form elementary molecules) or of another kind (to form compound molecules). White arsenic, As_2O_3, is a compound of the metal arsenic with oxygen; if through a solution of this compound hydrogen gas be allowed to pass, no chemical change takes place. If, however, hydrogen be generated or set free in a solution of white arsenic, then the hydrogen atoms, *while in the nascent state*, have sufficient energy to combine with both the elements arsenic and oxygen, forming arsenetted hydrogen or arsin, AsH_3, and water, H_2O.

Chemical reaction in its broader sense refers to any chemical change, but is used more especially when the intention is to study the nature of the substances decomposed or formed. The expression *reagent* is applied to those substances used for bringing about such changes.

Analysis and synthesis. These terms refer to two methods of research in chemistry, accomplished by two kinds of reaction, analytical and synthetical.

Analysis is that mode of research by which compound substances are broken up into their elements or into simpler forms of combination, and analytical reactions are all chemical processes by which the nature of an element, or of a group of elements, may be recognized.

Synthesis is that method of research by which bodies are made to unite to produce substances more complex.

Analytical and synthetical methods, or reactions, frequently blend into one another. This means: A reaction made with the intention of recognizing a substance may at the same time produce some compound of interest from a synthetical point of view.

Acids. The many compounds formed by the union of elements are so various in their nature, that no system of classification proposed up to the present time can be called perfect. There are, however, a few groups or classes of compounds, the properties of which are so well marked, that a substance belonging to either of them may be easily recognized. These groups are the acids, bases, and neutral substances.

Acids are characterized by the following properties:

1. They have (when soluble in water) an acid or sour taste.
2. They change the color of many organic substances, for instance of litmus, from blue to red.
3. They contain hydrogen, which can be replaced by metals, the compound thus formed being a salt.

According to the number of hydrogen atoms replaceable by metals, we distinguish monobasic, dibasic, and tribasic acids. Hydrochloric acid, HCl, is a monobasic, sulphuric acid, H_2SO_4, is a dibasic, phosphoric acid, H_3PO_4, is a tribasic acid.

Bases or **basic substances** show properties which are chemically opposite to those of acids. These properties are:

1. They have (when soluble in water) the taste of lye, or an alkaline taste.
2. They have (when soluble in water) an alkaline reaction, *i. e.*, they restore the color of organic substances when previously changed by acids, for instance that of litmus, from red to blue.
3. When acted upon by acids, they form salts. For instance: Potassium hydroxide is a base; when brought in contact with hydrochloric acid it forms water and the salt potassium chloride:

$$KOH + HCl = H_2O + KCl.$$

Neutral substances. All substances having neither acid nor basic properties are neutral. Water, for instance, is a neutral substance, having no acid or alkaline taste, and no action on red or blue litmus. Many neutral substances, to some extent even water, appear to possess the characteristic properties of both classes, acids and bases; of neither class, however, to a very great extent.

Salts. Salts are acids in which hydrogen has been replaced by metals or by basic radicals; a salt may be formed by the union of an acid and a base (usually with the simultaneous formation of water), or by the action of an acid on a metal (usually with the liberation of hydrogen).

For instance:

$$\underset{\text{Sodium hydroxide.}}{NaOH} + \underset{\text{Nitric acid.}}{HNO_3} = \underset{\text{Sodium nitrate.}}{NaNO_3} + \underset{\text{Water.}}{H_2O.}$$

$$\underset{\text{Iron.}}{Fe} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Ferrous sulphate.}}{FeSO_4} + \underset{\text{Hydrogen.}}{H_2.}$$

The process of combining an acid with a base in such a proportion that the acid and alkaline reactions disappear, and a neutral salt is formed, is known as *neutralization.*

According to the number of hydrogen atoms replaced in an acid, we distinguish normal and acid salts. A *normal salt* is one formed by the replacement of all the replaceable hydrogen atoms of an acid. For instance: Potassium chloride, KCl, potassium sulphate, K_2SO_4, potassium phosphate, K_3PO_4. (As monobasic acids have but one atom of hydrogen which can be replaced, they form normal salts only.)

Normal salts often have a neutral reaction to litmus, but they may have an acid, or even an alkaline reaction.

Acid salts are acids in which there has been replaced only a portion of their replaceable hydrogen atoms. For instance: $KHSO_4$, K_2HPO_4, KH_2PO_4

Basic salts are salts containing a higher proportion of a base than is necessary for the formation of a normal salt. Instances are basic mercuric sulphate, $HgSO_4.(HgO)_2$, basic lead nitrate, $Pb(NO_3)_2.Pb(OH)_2$. According to modern views basic salts are looked upon as derived from bases by replacement of part of their hydrogen by acid radicals. In the base lead hydroxide, $Pb(OH)_2$, one of the hydrogen atoms may be replaced by the radical of nitric acid, when basic lead nitrate, $Pb\begin{smallmatrix}NO_3\\ OH\end{smallmatrix}$, is formed.

In bismuth hydroxide, $Bi(OH)_3$, one, two, or three hydrogen atoms may be replaced by nitric acid, when the salts $Bi\begin{smallmatrix}\diagup NO_3\\ \diagdown (OH)_2\end{smallmatrix}$, $Bi\begin{smallmatrix}\diagup (NO_3)_2\\ \diagdown OH\end{smallmatrix}$ and $Bi(NO_3)_3$ are formed. The first two compounds are basic salts, while the third one is the normal salt.

Double salts are salts formed by replacement of hydrogen in an acid by more than one metal. For instance: Potassium-sodium sulphate, $KNaSO_4$.

Residue, radical, or compound radical, are expressions for unsaturated groups of atoms known to enter as a whole into different compounds, but having no separate existence. For instance: The bivalent oxygen combines with two atoms of the univalent hydrogen, forming the saturated compound H_2O, water. If we take from this H_2O one atom of H, there is left the group of atoms HO (now generally written OH), consisting of an atom of oxygen in which but one point of attraction is actually saturated, the second one not being provided for.

This group, OH, is a residue or radical, and is known to enter into many compounds; it is, for instance, a constituent of all the different hydroxides (formerly called hydrates), such as potassium hydroxide, KOH, calcium hydroxide, $ca(OH)_2$, etc.

According to the number of points of attraction left unprovided for in a radical, we distinguish univalent, bivalent, trivalent, and quadrivalent radicals.

Carbon is a quadrivalent element forming with the univalent hydrogen the saturated compound CH_4. By removal of one, two, or three hydrogen atoms the radicals CH_3', CH_2'', CH''', are formed.

9. GENERAL REMARKS REGARDING ELEMENTS.

Relative importance of different elements. Of the total number of about sixty-nine elements, comparatively but few (about one-fourth) are of great and general importance for the earth, and the phenomena taking place upon it. These important elements form the greater part of the mass of the solid portion of the earth, and of the water and atmosphere, and of all animal and vegetable matter.

QUESTIONS.—71. What physical actions have a tendency to decompose compound substances? 72. Explain the terms reaction and reagent. 73. Mention some instances of decomposition produced by the action of one substance upon another substance. 74. Why can no general rules be established in regard to the amount of attraction which different elements have for each other? 75. What is the difference between analytical and synthetical methods? 76. Define an acid, and state the general properties of basic and neutral substances. By what means can they be recognized? 77. Distinguish between mono-, di-, and tri-basic acids. 78. What are salts and how are they formed? 79. Define neutral, acid, and double salts. 80. Explain the term radical or residue.

Another number of elements are of less importance, because either they are not found in any large quantity, or do not take any active or essential part in the formation of organic matter; yet they are of interest and importance on account of being used, in their elementary state or in the form of different compounds, in every-day life for various purposes.

A third number of elements are found in such minute quantities in nature that they are almost exclusively of scientific interest. Even the existence of some elements, the discovery of which has been claimed, is doubtful.

The elements enumerated in column I. are those of great and general interest; in II. those claiming interest on account of the special use made of them; in III. those having scientific interest only.

I.	II.	III.
Aluminum	Antimony	Beryllium (Glucinum)
Calcium	Arsenic	Cæsium
Carbon	Barium	Columbium (Niobium)
Chlorine	Bismuth	Didymium
Hydrogen	Boron	Erbium
Iron	Bromine	Gallium
Magnesium	Cadmium	Germanium
Nitrogen	Cerium	Indium
Oxygen	Chromium	Iridium
Phosphorus	Cobalt	Lanthanum
Potassium	Copper	Osmium
Silicon	Fluorine	Palladium
Sodium	Gold	Rhodium
Sulphur	Iodine	Rubidium
	Lead	Ruthenium
	Lithium	Samarium
	Manganese	Scandium
	Mercury	Selenium
	Molybdenum	Tantalum
	Nickel	Tellurium
	Platinum	Terbium
	Silver	Thallium
	Strontium	Thorium
	Tin	Titanium
	Zinc	Tungsten
		Uranium
		Vanadium
		Ytterbium
		Yttrium
		Zirconium

Classification of elements may be based upon either physical or chemical properties, or upon a consideration of both. A natural classification of all elements is the one dividing them into two groups of metals and non-metals.

Metals are all elements which have that peculiar lustre known as metallic lustre; which are good conductors of heat and electricity; which, in combination with oxygen, form compounds generally showing basic properties; and which are capable of replacing hydrogen in acids, thus forming salts.

Non-metals or metalloids are all elements not having the above-mentioned properties. Their oxides in combination with water generally have acid properties. In all other respects the chemical and physical properties of non-metals differ widely. Their number amounts to 14, the other 55 elements being metals.

Natural groups of elements. Besides classifying all elements into metals and non-metals, certain members of both classes exhibit so much resemblance in their properties, that many of them have been arranged into natural groups. The members of such a natural group frequently show some connection between atomic weights and properties.

Chlorine,	35.4	Sulphur,	32	Lithium,	7	Calcium,	40
Bromine,	80	Selenium,	78.8	Sodium,	23	Strontium,	87
Iodine,	126.5	Tellurium,	125	Potassium,	39	Barium,	137

Each three elements mentioned in the above four columns resemble each other in many respects, forming a natural group. The relation between the atomic weights will hardly be suspected by looking at the figures, but will be noticed at once by adding together the atomic weights of the first and last elements and dividing this sum by 2, when the atomic weights (very nearly, at least) of the middle members of the series are obtained. Thus:

$$\frac{35.4 + 126.5}{2} = 81; \quad \frac{32 + 125}{2} = 78.5; \quad \frac{7 + 39}{2} = 23; \quad \frac{40 + 137}{2} = 88.5.$$

Mendelejeff's periodic law.[1] The relationship between atomic weights and properties has been used for arranging all elements systematically in such a manner that the existing relation is clearly pointed out. Of the various schemes proposed, the one arranged by Mendelejeff may be selected as most suitable to show this relation.

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[1] The consideration of this law should be postponed until the student has become acquainted with the larger number of important elements.

Looking at Mendelejeff's table on page 64, it will be seen that all the elements are arranged in the order of their atomic weights, and that the latter increase gradually by only a unit or a few units. Moreover, the arrangement is such that eight groups and twelve series are formed. The remarkable features of this classification may thus be stated: Elements which are more or less closely allied in their physical and chemical properties are made to stand together in a group, as may be seen by pointing out a few of the more generally known instances as found in the groups I., II., and VII., the first one containing the alkali metals, the second, the metals of the alkaline earths, the last the halogens.

There is, moreover, to be noticed a periodic repetition in the properties of the elements arranged in the horizontal lines from left to right. Leaving out group VIII. for the present, we find that the power of the elements to combine with oxygen atoms increases regularly from the left to the right, whilst the power of the elements to combine with hydrogen atoms increases from the right to left, as may be shown by the following instances:

I.	II.	III.	IV.	V.	VI.	VII.
Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
Hydrogen compounds unknown			SiH_4	PH_3	SH_2	ClH

The oxides on the left show strongly basic properties, as illustrated by sodium oxide; these basic properties become weaker in the second, and still weaker in the third group; the oxides of the fourth group show either indifferent, or but slightly acid properties, which latter increase gradually in the fifth, sixth, and seventh groups.

While some elements show an exception, it may be stated that most of the elements of group I. are univalent, of II. bivalent, of III. trivalent, of IV. quadrivalent, of V. quinquivalent, of VI. sexivalent, and of VII. septivalent.

Properties other than those above mentioned might be enumerated in order to show the regular gradation which exists between the members of the various series, but what has been pointed out will suffice to prove that there exists a regular gradation in the properties of the elements belonging to the same series, and that the same change is repeated in the other series, or that *the changes in the properties of elements are periodic.* It is for this reason that a series of elements is called a *period* (in reality a small period, in order to distinguish it from a large period, an explanation of which term will be given directly).

The 12 series or periods given in the following table show another

Periodic System.[1]

Series	Group I.	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VII.	Group VIII.
	— R_2O	— RO	— R_2O_3	RH_4 RO_2	RH_3 R_2O_5	RH_2 RO_3	RH R_2O_7	— RO_4?
1	H, 1	—	—	—	—	—	—	
2	Li, 7	Be, 9	B, 11	C, 12	N, 14	O, 16	F, 19	
3	Na, 23	Mg, 24	Al, 27	Si, 28	P, 31	S, 32	Cl, 35	
4	K, 39	Ca, 40	Sc, 44	Ti, 48	V, 51	Cr, 52	Mn, 55	Fe, 56. Ni, 59. Co, 59
5	(Cu, 63)	Zn, 65	Ga, 70	Ge, 72	As, 75	Se, 79	Br, 80	
6	Rb, 85	Sr, 87	Y, 89	Zr, 90	Nb, 94	Mo, 96	—	Ru, 101. Rh, 103. Pd, 106
7	Ag, 108	Cd, 112	In, 114	Sn, 119	Sb, 120	Te, 125	I, 127	
8	Cs, 133	Ba, 137	La, 133	Ce, 140	Di, 142	Tb, 159	—	— — —
9	—	—	—	—	Er, 166	—	—	
10	—	—	Yb, 173	—	Ta, 182	W, 184	—	Os, 190. Ir, 192. Pt, 194
11	(Au, 196)	Hg, 200	Tl, 204	Pb, 206	Bi, 209	—	—	
12	—	—	—	Th, 2 2	—	U, 239	—	— — —

---

[1] The decimals are omitted in giving the atomic weights.

highly characteristic feature, which consists in the fact that the corresponding members of the even (2, 4, 6, etc.) periods and of the uneven (3, 5, 7, etc.) periods resemble each other more closely than the members of the even periods resemble those of the uneven periods. Thus the metals calcium, strontium, and barium, of the even periods, 4, 6, and 8, resemble each other more closely than they resemble the metals magnesium, zinc, and cadmium, of the uneven periods, 3, 5, and 7, the latter metals again resembling each other greatly in many respects.

It is for this reason that in the table the elements belonging to one group are not placed exactly underneath each other, but are divided into two lines containing the members of even and uneven periods separately, whereby the elements resembling each other most are made to stand together.

In arranging the elements by the method indicated, it was found that the elements mentioned in group VIII. could not be placed in any of the 12 small periods, but that they had to be kept separately in a group by themselves, three of these metals always forming an intermediate series following the even periods 4, 6, and 10.

An uneven and even series, together with an intermediate series, form a *large period*, the number of elements contained in a complete large period being, therefore, $7 + 7 + 3 = 17$.

An *apparently* objectionable feature is the incompleteness of the table, many places being left blank; but it is this very point which renders the table so highly interesting and valuable.

Mendelejeff, in arranging his scheme, claimed that the places left blank belonged to elements not yet discovered, and he predicted not only the existence of these as yet missing elements, but also described their properties. Fortunately his predictions have, in at least three cases, been verified, three of the missing elements having since been discovered, and named, *scandium*, *gallium*, and *germanium*. These elements not only fitted in the previously blank spaces by virtue of their atomic weights, but their general properties also assigned to them the places which they now occupy.

Physical properties of elements. Most elements are, at the ordinary temperature, solid substances, two are liquids (bromine and mercury), five are gases (oxygen, hydrogen, nitrogen, chlorine, and fluorine). Most of the solid elements may be converted into liquids and gases by the action of heat. Some solid elements, however, have so far resisted all attempts to change their state of aggregation, as, for instance, carbon.

Most, if not all, of the solid elements may be obtained in the crystallized state; a few are amorphous and crystallized, or polymorphous. The physical properties of many elements in these different states differ widely. For instance: Carbon is known crystallized as diamond and graphite, or amorphous as charcoal. The property of elements to assume such different conditions is called *allotropy*, and the different forms of an element are termed *allotropic modifications.*

Some of the gaseous elements are also capable of existing in allotropic modifications. For instance: Oxygen is known as such and as ozone, the latter differing from the common oxygen both in its physical and chemical properties. The explanation given for this surprising fact, that one and the same element has different properties in certain modifications, is, that either the molecules or the atoms within the molecules are arranged differently. Ozone, for instance, has three atoms of oxygen in the molecule, while the common oxygen molecule contains but two atoms.

Most of the elements are tasteless and odorless; a few, however, have a distinct odor and taste, as, for instance, iodine and bromine.

Relationship between elements and the compounds formed by their union. The properties of the compounds formed by the combination of elements are so various that it is next to impossible to give any general rule by which they may be indicated. It may be said, however, that nearly all of the gaseous compounds contain at least one gaseous element, and that solid elements, when combining with each other, generally form solid substances, rarely liquids, and never compounds showing the gaseous state at the ordinary temperature.

Nomenclature. The chemical nomenclature of compound substances has undergone considerable changes within the last twenty years. These changes were made in conformity with our present views of the constitution of the compounds.

When two elements combine in one proportion only, little difficulty is experienced in the formation of a name, as, for instance, in iodide of potassium or potassium iodide, KI, chloride of sodium or sodium chloride, $NaCl$.

When two elements combine in more than one proportion, the syllables, *mono*, *di*, *tri*, *tetra*, and *penta* are frequently used to designate the relative quantity of the elements. For instance: Carbon *mon*oxide, CO, carbon *di*oxide, CO_2, phosphorus *tri*chloride, PCl_3, phosphorus *penta*chloride, PCl_5.

In many cases the syllables *ous* and *ic* are used to distinguish the proportions in which two elements combine; the syllable *ous* being used for the simpler or lower, the syllable *ic* for the more complex or higher form of combination. For instance: Phosphor*ous* chloride, PCl_3, and phosphor*ic* chloride, PCl_5; ferr*ous* oxide, FeO, ferr*ic* oxide, Fe_2O_3.

The syllables *mono* and *sesqui* also are used occasionally to mark this difference, as, for instance, *mon*oxide of iron, FeO, *sesqui*oxide of iron, Fe_2O_3.

When two oxides of the same element ending in *ous* and *ic* form acids (by entering in combination with water), the same syllables are used to distinguish these acids. Phosphor*ous* oxide, P_2O_3, forms phosphor*ous* acid; phosphor*ic* oxide, P_2O_5, forms phosphor*ic* acid.

The salts formed by these acids are distinguished by using the syllables *ite* and *ate*. Phosph*ite* of sodium is derived from phosphorous acid, phosph*ate* of sodium from phosphoric acid. Sulph*ites* and sulph*ates* are derived from sulphurous and sulphuric acid, respectively.

According to the new nomenclature, the name of the metal precedes that of the acid or acid radical in an acid. For instance, sodium phosphite, instead of phosphite of sodium; potassium sulphate, instead of sulphate of potassium. The acids themselves are looked upon as hydrogen salts, and are sometimes named accordingly: hydrogen nitrate for nitric acid, hydrogen chloride for hydrochloric acid, etc.

When the number of elements and the number of atoms increase in the molecule, the names become in most cases more complicated. The rules applied to the formation of such complicated names will be spoken of later.

Writing chemical equations. It has been shown that chemical changes are expressed in chemical equations by means of symbols. These equations are formed by placing the molecules which are to act upon one another, and which are called *factors* and are connected by the sign +, to the left of the sign of equality, and by placing the molecule or molecules which result from the decomposition, and are called *product* or *products*, to the right of the sign of equality, connecting them also by the + sign if more than one product be formed.

Every correct chemical equation is correct mathematically also—*i. e.*, the sum of the atoms as well as that of the molecular weights of the factors equals the sum of the atoms and that of the molecular weights of the products respectively. For instance: Sodium carbonate and calcium chloride form calcium carbonate and sodium chloride. Expressed in chemical equation we say:

$$\text{Na}_2\text{CO}_3 + \text{CaCl}_2 = \text{CaCO}_3 + 2\text{NaCl}.$$

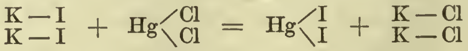
Sodium carbonate and calcium chloride are the factors, calcium carbonate and sodium chloride the products. Adding together the molecular weights of the factors and those of the products we find equal quantities, as follows:

$$\begin{array}{rcrcrcrcr}
2\text{Na} = 46 & & \text{Ca} = 40 & & & \qquad & \text{Ca} = 40 & & 2\text{Na} = 46 \\
\text{C} = 12 & & 2\text{Cl} = 71 & & & & \text{C} = 12 & & 2\text{Cl} = 71 \\
3\text{O} = 48 & & & & & & 3\text{O} = 48 & & \\
\hline
106 & + & 111 & = 217 & & & 100 & + & 117 = 217
\end{array}$$

Chemical equations not only are used for representing chemical changes, but also are the starting-point in all the chemical calculations in which the quantities of substances entering into chemical actions, or the quantities of the product formed, are concerned.

The above calculation teaches, for instance, that 106 parts by weight of sodium carbonate are acted upon by 111 parts by weight of calcium chloride, and that 100 parts by weight of calcium carbonate and 117 parts by weight of sodium chloride are formed by this action. These data may, of course, be utilized to find how much calcium chloride may be needed for the decomposition of one pound or of any other definite weight of sodium carbonate; or how much of these two substances may be required to produce one hundred pounds, or any other definite weight, of calcium carbonate.

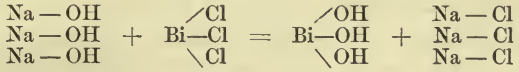
While in many cases of chemical decomposition the change which is to take place cannot be foretold, but has to be studied experimentally, there are other chemical changes which can be predicted with certainty (see Chapter 8, page 56). In the latter case especially there is no difficulty in writing out the change in the form of an equation. *In doing this it must be borne in mind that equivalent quantities replace one another;* that, for instance, two atoms of a univalent element are required to replace one atom of a bivalent element, as, for instance, in the case of the decomposition taking place between potassium iodide and mercuric chloride, when two molecules of the first are required to decompose one molecule of the second compound:



or

$$2\text{KI} + \text{HgCl}_2 = \text{HgI}_2 + 2\text{KCl}.$$

Whenever the exchange of atoms takes place between univalent and trivalent elements, three of the first are required for one of the second, as in the case of the action of sodium hydroxide on bismuth chloride:



$$\begin{matrix} Na-OH \\ Na-OH \\ Na-OH \end{matrix} + Bi\begin{matrix} /Cl \\ -Cl \\ \backslash Cl \end{matrix} = Bi\begin{matrix} /OH \\ -OH \\ \backslash OH \end{matrix} + \begin{matrix} Na-Cl \\ Na-Cl \\ Na-Cl \end{matrix}$$

or

$$3NaOH + BiCl_3 = Bi(OH)_3 + 3NaCl.$$

In the following examples of double composition an exchange takes place between the atoms of metallic elements, or between the metallic elements and the hydrogen. The student, in completing the equations, has also to select the correct quantity, *i. e.*, the correct number of molecules of the factors required for the change. The interrogation marks indicate that more than one atom or one molecule of the substance is needed for the reaction.

$Na' + H'Cl =$

$H_2'SO_4 + K'(?) =$

$Ca'' + H'Cl\,(?) =$

$Fe'' + H_2'SO_4 =$

$H'Cl + Ag'NO_3 =$

$Ca''Cl_2 + Ag'NO_3(?) =$

$Bi'''Cl_3 + Ag'NO_3(?) =$

$Cu''SO_4 + H_2'S =$

$Ba''Cl_2 + Na_2'SO_4 =$

$Na_2'CO_3 + H_2'SO_4 =$

$Bi'''(NO_3)_3 + K'OH\,(?) =$

$Al_2'''(SO_4)_3 + K'OH\,(?) =$

$Al_2'''(SO_4)_3 + Ca''(OH)_2(?) =$

$Fe_2'''Cl_6 + Ag'NO_3\,(?) =$

How to study chemistry. In studying chemistry, the student is advised to impress upon his memory five points regarding every important element or compound. These points are:

1. *Occurrence in nature.* Whether in free or combined state; whether in the air, water, or solid part of the earth.
2. *Mode of preparation* by artificial means.
3. *Physical properties.* State of aggregation and influence of heat upon it; color, odor, taste, solubility, etc.
4. *Chemical properties.* Atomic and molecular weight; valence; amount of attraction toward other elements or compounds; acid, alkaline, or neutral reaction; reactions by which it may be recognized and distinguished from other substances.
5. *Application and use* made of it in every-day life, in the arts, manufactures, or medicine.

Of the most important elements and compounds, the history of their discovery, and, occasionally, some special points of interest, should be noticed also.

All students having the facility for working in a chemical laboratory are strongly advised to make all those experiments and reactions which will be mentioned in connection with the different substances to be considered in this book.

By adopting this mode of studying chemistry the student will soon acquire a fair knowledge of chemical facts, yet he might know little of the science of chemistry. In order to acquire this latter knowledge he should study not only facts, but also the relationship existing between them and between the laws governing the phenomena connected with these facts. It is by this method only that the science of chemistry can be successfully mastered.

QUESTIONS.—81. Why are not all the elements of equal importance? 82. State the physical and chemical properties of metals. 83. How are metals distinguished from non-metals? 84. What relation often exists between the atomic weights of elements belonging to the same group? 85. Explain the term allotropic modification. 86. Mention some elements capable of existing in allotropic modifications. 87. What relation exists between the properties of elements and the properties of the compounds formed by their union? 88. In which cases are the syllables mono-, di-, tri-, tetra-, and penta- used in chemical nomenclature? 89. What use is made of the syllables *ous* and *ic*, *ite* and *ate*, in distinguishing compounds from each other? 90. What are the principal features of the periodic law?

III.

NON-METALS AND THEIR COMBINATIONS.

THE total number of the non-metals is fourteen; two of them, selenium and tellurium, are of so little importance that they will be but briefly considered in this book.

Symbols, atomic weights, and derivation of names.

Boron,	B	=	10.9.	From *borax*, the substance from which boron was first obtained.
Bromine,	Br	=	79.8.	From the Greek *βρῶμος* (bromos), stench, in allusion to the intolerable odor.
Carbon,	C	=	12.	From the Latin *carbo*, coal, which is chiefly carbon.
Chlorine,	Cl	=	35.4.	From the Greek *χλωρός* (chloros), green, in allusion to its green color.
Fluorine,	F	=	19.	From *fluorspar*, the mineral calcium fluoride, used as flux (*fluo*, to flow.)
Hydrogen,	H	=	1.	From the Greek *ὕδωρ* (hudor), water, and *γεννάω* (gennao), to generate.
Iodine,	I	=	126.5.	From the Greek *ἴον* (ion), violet, referring to the color of its vapors.
Nitrogen,	N	=	14.	From the Greek *νίτρον* (nitron), nitre, and *γεννάω* (gennao), to generate.
Oxygen,	O	=	16.	From the Greek *ὀξύς* (oxus), acid, and *γεννάω* (gennao), to generate.
Phosphorus,	P	=	31.	From the Greek *φῶς* (phos), light, and *φέρειν* (pherein), to bear.
Silicon,	Si	=	28.3.	From the Latin *silex*, flint, or silica, the oxide of silicon.
Sulphur,	S	=	32.	From *sal*, salt, and *πῦρ* (pur), fire, referring to the combustible properties of sulphur.

State of aggregation.

Under ordinary conditions the non-metals show the following states:

Gases.		*Liquids.*	B. P.	*Solids.*	F. P.	B. P.
Hydrogen, Oxygen, Nitrogen,	Are converted into liquids with difficulty.	Bromine,	63° C.	Phosphorus,	44° C.	280° C.
				Iodine,	107	175
				Sulphur,	111	400
Chlorine,	Easily liquefied.			Carbon, Boron, Silicon,	Infusible.	
Fluorine,	?					

Occurrence in nature.

a. In a free or combined state.

Carbon in coal, organic matter, carbon dioxide, carbonates.
Nitrogen in air, ammonia, nitrates, organic matter.
Oxygen in air, water, organic matter, most minerals.
Sulphur chiefly as sulphates and sulphides.

b. In combination only.

Boron in boric acid and borax.
Bromine in salt wells and sea-water as magnesium bromide, etc.
Chlorine as sodium chloride in sea-water, etc.
Fluorine as calcium fluoride, fluorspar.
Hydrogen in water and organic matter.
Iodine as iodides in sea-water.
Phosphorus as phosphate of calcium, iron, etc., in bones and rocks.
Silicon as silicic acid or silica, and in silicates.

Time of discovery.

Sulphur, Carbon, Long known in the elementary state; recognized as elements in the latter part of the eighteenth century.
Phosphorus, 1669, by Brandt, of Germany.
Chlorine, 1770, by Scheele, of Sweden.
Nitrogen, 1772, by Rutherford, of England.
Oxygen, 1774, by Priestley, of England, and Scheele, of Sweden.
Hydrogen, 1781, by Cavendish, of England.
Boron, 1808, by Gay-Lussac, of France.
Fluorine, 1810, by Ampère, of France.
Iodine, 1812, by Courtois, of France.
Silicon, 1823, by Berzelius, of Sweden.

Valence.

Univalent.	*Bivalent.*	*Trivalent or quinquivalent.*	*Quadrivalent.*
Hydrogen,	Oxygen,	Nitrogen,	Carbon,
Chlorine,	Sulphur.	Boron,	Silicon.
Bromine,		Phosphorus.	
Iodine,			
Fluorine.			

10. OXYGEN.

$O^{ii} = 16$ (15.96).

History. Oxygen was discovered in the year 1774 by Priestley, in England, and Scheele, in Sweden, independently of each other; its true nature was soon afterward recognized by Lavoisier, of France, who gave it the name oxygen, from the two Greek words, ὀξύς (oxus), acid, and γεννάω (gennao), to produce or generate. Oxygen means, consequently, generator of acids.

Occurrence in nature. There is no other element on our earth present in so large a quantity as oxygen. It has been calculated that not less than about one-third, possibly as much as 45 per cent., of the total weight of our earth is made up of oxygen; it is found in a free or uncombined state in the atmosphere, of which it forms about one-fifth of the weight. Water contains eight-ninths of its weight of oxygen, and most of the rocks and different mineral constituents of our earth contain oxygen in quantities varying from 30 to 50 per cent.; finally, it is found as one of the common constituents of most animal and vegetable matters.

If the unknown interior of our earth should be similar in composition to the solid crust of mineral constituents which have been analyzed, then the subjoined table will give approximately the proportions of those elements present in the largest quantity.

Oxygen	45 parts.	Calcium	4 parts.
Silicon	28 "	Magnesium	2 "
Aluminum	8 "	Sodium	2 "
Iron	6 "	Potassium	2 "

Preparation. The oxides of the so-called noble metals (gold, silver, mercury, platinum) are by heat easily decomposed into the metal and oxygen:

$$HgO = Hg + O;$$
$$Ag_2O = 2Ag + O.$$

A more economical method of obtaining oxygen is the decomposition of potassium chlorate, $KClO_3$, into potassium chloride, KCl, and oxygen by application of heat:

$$KClO_3 = KCl + 3O.$$

While the above formula represents the final result of the decomposition, it takes place actually in two stages. At first potassium chlorate gives up but one-third of its total oxygen, forming potassium chloride and perchlorate, $KClO_4$, thus:

$$2KClO_3 = KClO_4 + KCl + 2O.$$

This part of the decomposition takes place at a comparatively low temperature; after it is complete, the temperature rises considerably and the decomposition of the perchlorate begins:

$$KClO_4 = KCl + 4O.$$

If the potassium chlorate be mixed with 30–50 per cent. of manganese dioxide, and this mixture be heated, the liberation of oxygen takes place with greater facility and at a lower temperature than by heating potassium chlorate alone. Apparently, the manganese dioxide takes no active part in the decomposition, as its total amount is found in an unaltered condition after all potassium chlorate has been decomposed by heat. A satisfactory explanation regarding this action of manganese dioxide is yet wanting.

A third method is to heat to redness, in an iron vessel, manganese dioxide (MnO_2), which suffers then a partial decomposition:

$$3MnO_2 = Mn_3O_4 + 2O.$$

In this case there is liberated but one-third of the total amount of oxygen present, while two-thirds remain in combination with the manganese.

Other methods of obtaining oxygen are: Decomposition of water by electricity, heating of dichromates, nitrates, barium dioxide, and other substances, which evolve a portion of the oxygen contained in the molecules.

Heating a concentrated solution of bleaching powder with a small quantity of a cobalt salt (cobaltous chloride) furnishes a liberal supply of oxygen, the calcium hypochlorite of the bleaching powder being decomposed into calcium chloride and oxygen:

$$Ca(ClO)_2 = CaCl_2 + 2O.$$

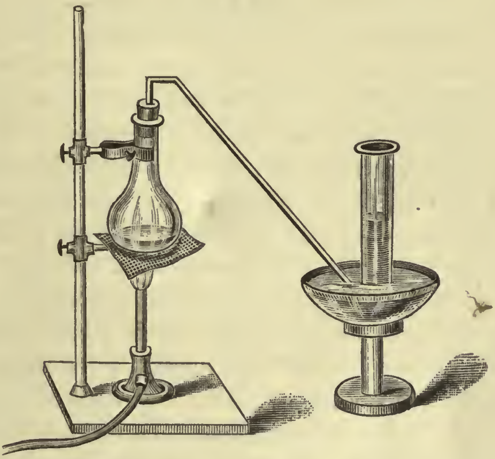
Oxygen may be obtained at the ordinary temperature by adding water to a mixture of powdered potassium ferricyanide and barium dioxide, and also by the decomposition of potassium permanganate and hydrogen dioxide in the presence of dilute sulphuric acid.

Experiment 1. Generate oxygen by heating a small quantity (about 5 grammes) of potassium chlorate in a dry flask of about 100 c.c. capacity, to which, by means of a perforated cork, a bent glass tube has been attached, which leads under the surface of water contained in a dish. (Fig. 6.) Collect the gas by placing over the delivery-tube large test-tubes (or other suitable vessels) filled with water. Notice that a strip of wood, a wax candle, or any other substance which burns in air, burns with greater energy in oxygen, and that an extinguished taper, on which a spark yet remains, is rekindled when placed in oxygen gas. Notice, also, the physical properties of the gas. How many c.c. of oxygen can be obtained from 5 grammes of potassium chlorate? 1000 c.c. of oxygen weigh 1.43 grammes.

The quantity of oxygen liberated from a given quantity of a substance may be easily calculated from the atomic and molecular weights of the substance or substances suffering decomposition. For instance: 100 pounds of oxygen may be obtained from how many pounds of potassium chlorate, or from how many pounds of manganese dioxide?

The molecular weight of potassium chlorate is found by adding together the weights of 1 atom of potassium = 39 + 1 atom of chlorine = 35.4 + 3 atoms of oxygen = 48; total = 122.4. Every 122.4 parts by weight of potassium chlorate liberate the weight of 3 atoms, or 48 parts by weight, of oxygen. If 48 are obtained from 122.4, 100 are obtained from 255.

FIG. 6.



Apparatus for generating oxygen.

$$48 : 122.4 :: 100 : x$$
$$x = 255.$$

In a similar manner, it will be found that 813.7 pounds of manganese dioxide are necessary to produce 100 pounds of oxygen. $MnO_2 = 54.8 + 32 = 86.8$. $3MnO_2 = 3 \times 86.8 = 260.4$. Every 260.4 parts furnish $2 \times 16 = 32$ parts of oxygen.

$$32 : 260.4 :: 100 : x$$
$$x = 813.7.$$

Physical properties. Oxygen is a colorless, inodorous, tasteless gas; up to a few years ago it was looked upon as a permanent or stable gas, as all attempts to liquefy or solidify it had failed. Lately, however, these efforts have been successful, and oxygen has been converted (though in small quantities) into a colorless liquid by the application of a pressure of 470 atmospheres at a temperature of —130° C. (—202° F.)

Oxygen is but sparingly soluble in water (about 3 volumes in 100 at common temperature). A litre of oxygen under 760 mm. pressure, and at the temperature 0° C. (32° F.), weighs 1.4298 grammes.

Chemical properties. The principal feature of oxygen is its great affinity for almost all other elements, both metals and non-metals; with nearly all of which it combines in a direct manner. The more important elements with which oxygen does not combine directly are: Cl, Br, I, F, Au, Ag, and Pt; but even with these it combines indirectly, excepting F.

The act of combination between other substances and oxygen is called *oxidation*, and the products formed, *oxides*. The large number of oxides are divided usually into three groups, and distinguished as *basic oxides* (sodium oxide, Na_2O, calcium oxide, CaO), *neutral oxides* (water, H_2O, manganese dioxide, MnO_2, lead dioxide, PbO_2), and *acid-forming* or *acidic oxides*, also called *anhydrides* (carbon dioxide, CO_2, sulphur trioxide, SO_3). Whenever the heat generated by oxidation (or by any other chemical action) is sufficient to cause the emission of light, the process is called *combustion*. Oxygen is the chief supporter of all the ordinary phenomena of combustion. Substances which burn in atmospheric air burn with greater facility in pure oxygen. This property is taken advantage of to recognize and distinguish oxygen from most other gases. Processes of oxidation evolving no light are called *slow combustion*. An instance of slow combustion is the combustion of the different organic substances in the living animal, the oxygen being supplied by respiration.

For a process of oxidation it is not absolutely necessary that free oxygen be present. Many substances contain oxygen in such a form of combination that they part with it easily when brought in contact with substances having a greater affinity for it. Such substances are called *oxidizing agents*, as, for instance, nitric acid, potassium chlorate, potassium permanganate, etc.

In all combustions we have at least two substances acting chemically upon one another, which substances are generally spoken of as combustible bodies and supporters of combustion. Illuminating gas is a combustible substance, and oxygen a supporter of combustion; but these terms are only relatively correct, since oxygen may be caused to burn in illuminating gas, whereby it is made to assume the position of a combustible substance, whilst illuminating gas is the supporter of combustion.

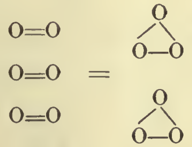
While some substances, such as iron and phosphorus, undergo slow combustion at the ordinary temperature, there is a certain degree of temperature, characteristic of each substance, at which it inflames. This point is known as *kindling temperature*, and varies widely in different substances. Zinc ethyl ignites at the ordinary temperature, phosphorus at 50° C. (122° F.), sulphur at about 450° C. (842° F.), carbon at a red heat, and iron at a white heat. The heat produced by the combustion is generally higher than the kindling temperature, and it is for this reason that a substance continues to burn until it is consumed, provided the supply of oxygen be not cut off, and the temperature be not through some cause lowered below the kindling temperature.

The total amount of heat evolved during the combustion of a substance is the same as that generated by the same substance when undergoing slow combustion, but the intensity depends upon the time required for the oxidation. A piece of iron may require years to combine with oxygen, and it may be burned up in a few minutes; yet the total heat generated in both cases is the same, though we can notice and measure it in the first instance by most delicate instruments only, while in the second it is very intense.

Ozone is an allotropic modification of oxygen, which is formed when non-luminous electric discharges pass through atmospheric air or through oxygen; when phosphorus, partially covered with water, is exposed to air, and also during a number of chemical decompositions. Ozone differs from ordinary oxygen by possessing a peculiar odor, by being an even stronger oxidizing agent than common oxygen, by liberating iodine from potassium iodide, etc. This latter action may be used for demonstrating the presence of ozone by suspending in the gas a paper moistened with a solution of potassium iodide and starch. The iodine, liberated by the ozone, forms with starch a dark-blue compound. Theoretically, we assume that ozone contains three, common oxygen but two, atoms in the molecule, which is substantiated by the fact that three volumes suffer a condensation to two volumes when converted into ozone, which would indicate that three molecules of oxygen furnish two molecules of ozone, thus:

$$3O_2 = 2O_3$$

or



Ozone occurs in small quantities in country air, but is rarely noticed in cities, where it is decomposed too quickly by the impurities of the atmospheric air. It has been assumed that ozone acts advantageously, as it has a tendency to destroy matters which are unwholesome. Too little, however, is known of the subject to justify a positive opinion in regard to it.

QUESTIONS.—91. By whom and at what time was oxygen discovered? 92. How is oxygen found in nature? 93. Mention three processes by which oxygen may be obtained. 94. How much oxygen may be obtained from 490 grammes of potassium chlorate? 95. State the physical and chemical properties of

11. HYDROGEN.

$H = 1.$

History. Hydrogen was obtained by Paracelsus in the 16th century; its elementary nature was recognized by Cavendish, in 1766. The name is derived from ὕδωρ (hudor), water, and γεννάω (gennao), to generate, in allusion to the formation of water by the combustion of hydrogen.

Occurrence in nature. Hydrogen is found chiefly as a component element of water; it enters into the composition of most animal and vegetable substances, and is a constituent of all acids. Small quantities of free hydrogen are found in the gases produced by the decomposition of organic matters (as, for instance, in the intestinal gases), and also in the natural gas escaping from the interior of the earth.

Preparation. Hydrogen may be obtained by passing an electric current through water previously acidified with sulphuric acid, by which it is decomposed into its elements:

$$H_2O = 2H + O.$$

A second process is the decomposition of water by metals. Some metals, such as potassium and sodium, decompose water at the ordinary temperature; whilst others, iron, for instance, decompose it at a red heat:

$$\begin{aligned} K + H_2O &= KOH + H; \\ Fe + H_2O &= FeO + 2H. \end{aligned}$$

A very convenient way of liberating hydrogen is the decomposition of dilute hydrochloric or sulphuric acid by zinc or iron:

$$Zn + 2HCl = \underset{\substack{\text{Zinc} \\ \text{chloride.}}}{ZnCl_2} + 2H;$$

$$Fe + H_2SO_4 = \underset{\substack{\text{Ferrous} \\ \text{sulphate.}}}{FeSO_4} + 2H.$$

Hydrogen may also be obtained by heating granulated zinc or

---

oxygen. 96. Explain the terms combustion, slow combustion, combustible substance, and supporter of combustion. 97. Mention some oxidizing agents. 98. What is ozone, and how does it differ from common oxygen? 99. Under what circumstances is ozone formed? 100. State the molecular weight of oxygen and ozone.

aluminum with strong solutions of potassium or sodium hydroxide, in which case the decomposition is explained thus:

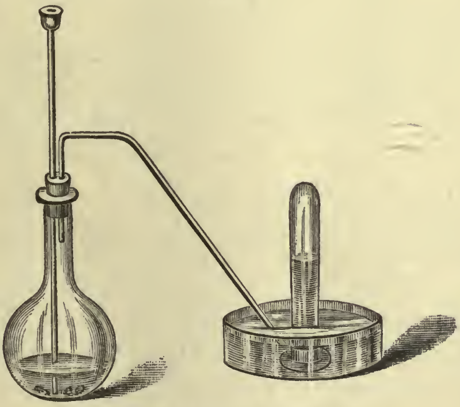
$$Zn + 2KOH = \underset{\text{Potassium zincate.}}{K_2ZnO_2} + 2H;$$

$$Al + 3NaOH = \underset{\text{Sodium aluminate.}}{Na_3AlO_3} + 3H.$$

Whenever hydrogen is generated, care should be taken to expel all atmospheric air from the vessel in which the generation takes place, before the hydrogen is ignited, as otherwise an explosion may result.

Experiment 2. Place a few pieces of granulated zinc (about 10 grammes) in a flask of about 200 c.c. capacity, which is arranged as shown in Fig. 7. Cover the zinc with water, and pour upon it through the funnel tube a little sulphuric acid, adding more when gas ceases to be evolved. Notice the effervescence around the zinc. Collect the gas in test-tubes over water and ignite it by taking the test-tube (with mouth downward) to a flame near by. Notice that the first portions of gas collected, which are a mixture of hydrogen and atmospheric air, explode when ignited in the test-tube, while the subsequent portions burn quietly. Pour the contents of one test-tube into another one by allowing the light hydrogen gas to rise into and replace the air in a test-tube held over the one filled with hydrogen. Take two test-tubes completely filled with the gas; hold one mouth upward, the other one mouth downward: notice that from the first one the gas escapes after a few seconds, while it remains in the second tube a few minutes, as may be shown by holding the tubes near a flame to cause ignition.

FIG. 7.



Apparatus for generating hydrogen.

After having ascertained that all atmospheric air has been expelled from the flask, the gas may be ignited directly at the mouth of the delivery tube, after moving it out of the water.

Experiment 3. Pour into a test-tube of not less than 50 c.c. capacity, 5 c.c. of hydrochloric acid, fill up with water, close the tube with the thumb and set it inverted into a porcelain dish partly filled with water. Weigh of metallic zinc 0.04 gramme, and bring it quickly under the mouth of the test-tube, so that the generated hydrogen rises in the tube. Prepare a second tube in the same manner, and introduce 0.04 gramme of metallic magnesium. In case the decomposition of the acids by the metals should proceed too slowly, a little more acid may be poured into the dishes.

When the metals are completely dissolved it will be seen that the volumes of hydrogen in the two tubes bear a relation to each other of about 10 to 27.

In order to measure the gas volumes as correctly as the simple apparatus permits, the tubes should be transferred to a large beaker filled with cold water, bringing the surfaces of the liquids in the test-tube and beaker on a level, and marking on the outside of the test-tubes (with a file or paper strip) the exact height of the gas.

After having emptied the test-tubes, they may be filled with water from a pipette or from a burette to the point which has been marked, and thus the exact volume of gas generated is ascertained.

Repeat the operation, using 0.065 gramme of zinc and 0.024 gramme of magnesium. Notice that in this case equal volumes of hydrogen are obtained. Calculate the weight of hydrogen from the cubic centimetres liberated, and compare this weight with the weights of zinc and magnesium used. What relation is there between the weights of the liberated hydrogen and the metals used, and the atomic weights of these three elements?

Properties. Hydrogen is a colorless, inodorous, tasteless gas; it is the lightest of all known substances, having a specific gravity of 0.0692 as compared with atmospheric air (= 1). One litre of hydrogen at 0° C. (32° F.), and a barometric pressure of 760 mm., weighs 0.0896 gramme, or one gramme occupies a space of 11.163 litres; 100 cubic inches weigh about 2.265 grains.

Hydrogen resists liquefaction more than any other gas. When subjected to a pressure of 650 atmospheres and a temperature of —150° C. (—238° F.), hydrogen forms a steel-blue liquid, a portion of which is converted into a solid on suddenly releasing the pressure, in consequence of the intense cold produced by the rapid evaporization of the liquefied hydrogen.

In its chemical properties, hydrogen resembles the metals more than the non-metals; it burns easily in atmospheric air, or in pure oxygen, with a non-luminous, colorless, or slightly bluish flame producing during this process of combustion a higher temperature than can be obtained by the combustion of an equal weight of any other substance.

$$H_2 + O = H_2O.$$

The formation of water by the combustion of hydrogen distinguishes it from other gases.

Two volumes of hydrogen combine with one volume of oxygen, forming two volumes of gaseous water.

Water, $H_2O = 18$. Hydrogen monoxide. Water is not found in nature in an absolutely pure state. The purest natural water is rain-water collected after the air has been purified from dust, etc., by previous rain. Comparatively pure water may be obtained by melting ice, since, when water containing impurities is frozen partially, these are mostly left in the uncongealed water.

The waters of springs, wells, rivers, etc., differ widely from each other; they all contain more or less of substances dissolved by the water in its course through the atmosphere or through the soil and rocks. The constituents thus absorbed by the water are either solids or gases.

Solids generally found in natural waters are common salt (sodium chloride), gypsum (calcium sulphate), and carbonate of lime (calcium carbonate); frequently found are chlorides and sulphates of potassium and magnesium, traces of silica and salts of iron. Gases absorbed by water are constituents of the atmospheric air, chiefly oxygen, nitrogen, and carbon dioxide. One hundred volumes of water contain about two volumes of nitrogen, one volume of oxygen, and one volume of carbon dioxide.

Mineral waters are spring waters containing one or more substances in such quantities that they impart to the water a peculiar taste and generally a decided medicinal action. According to the predominating constituents we distinguish *bitter* waters, containing larger quantities of magnesium salts; *iron* or *chalybeate* waters, containing carbonate or sulphate of iron; *sulphur* or *hepatic* waters, containing hydrogen sulphide; *effervescent* waters, containing large quantities of carbonic acid, etc.

Drinking-water. A good drinking-water should be free from color, odor, and taste; it should neither be an absolutely pure water, nor a water containing too much of foreign matter. Water containing from 2 to 4 parts of total inorganic solids (chiefly carbonate of lime and common salt) in 10,000 parts of water and about 1 volume of carbon dioxide in 100 volumes of water, may be said to be a good drinking-water. There are, however, good drinking-waters which contain more of total solids than the amount mentioned above.

Most objectionable in drinking-water are *organic substances,* especially when derived from animal matter, and more especially when in a state of decomposition, because such decomposing organic matter is frequently accompanied by living organisms (germs) which may cause disease. Boiling of water destroys these germs, and by subsequent filtering of the boiled water through sand, charcoal, spongy iron, etc., an otherwise unwholesome water may be rendered fit for drinking.

It should be remembered that no filter can remain efficient for any length of time, as the impurities of the water are retained by the materials used as a filter, and this may become, therefore, a source of pollution instead of a purifier. By heating to a low red heat the materials used for filtering, these are cleaned and may be used again. The methods applied to the analysis of drinking-water will be mentioned later. (See Index.)

Distilled water, Aqua destillata. The process for obtaining pure water is distillation in a suitable apparatus. From 1000 parts of water used for distillation, the first 100 parts distilled over should not be used, as they contain the gaseous constituents. The solids contained in the water are left in the undistilled portion, which should not be less than 200 parts.

Properties of water. Water is an inodorous, tasteless, and, in small quantities, colorless liquid. Thick layers of water show a blue color. It is perfectly neutral, yet it has a tendency to combine with both acid and basic substances. These compounds are usually called *hydroxides* (formerly *hydrates*), such as $NaOH$, $Ca(OH)_2$, etc. These compounds are often formed by direct union of an oxide with water, thus:

$$CaO + H_2O = Ca(OH)_2.$$

Water is the most common solvent, both in nature and in artificial processes. As a general rule, solids are dissolved more quickly and in larger quantities by hot water than by cold, but to this there are many exceptions. For instance: Common salt is nearly as soluble in cold as in hot water; sodium sulphate is most soluble in water of 33° C. (91° F.), and some calcium salts are less soluble in hot than in cold water.

Many salts combine with water in crystallizing; crystallized sodium sulphate, for instance, contains more than half its weight of water. This water is called *water of crystallization*, and is expelled generally at a temperature of 100° C. (212°F.). Some crystallized substances lose water of crystallization when exposed to the air; this property is known as *efflorescence*. Crystals of sodium carbonate, ferrous sulphate, etc., effloresce, as is shown by the formation of powder upon the crystalline surface. The term *deliquescence* is applied to the power of certain solid substances to absorb moisture from the air, thereby becoming damp or even liquid, as, for instance, potassium hydroxide, calcium chloride, etc. Such substances are spoken of also as being *hygroscopic*, and are used for drying gases.

Hydrogen dioxide, Hydrogen peroxide, H_2O_2. This compound may be obtained in aqueous solution by the action of carbonic acid (or other acids) on barium dioxide suspended in water, when barium carbonate and hydrogen dioxide are formed:

H2O2

$$BaO_2 + H_2O + CO_2 = BaCO_3 + H_2O_2.$$

The liquid, separated by decantation from the insoluble carbonate, may be concentrated under the receiver of an air-pump, and is, when thus obtained, a colorless liquid of a specific gravity 1.45, possessing remarkable bleaching and antiseptic properties. By higher temperatures, as well as by the action of many substances, it is readily decomposed into water and oxygen.

Solution of hydrogen dioxide, Aqua hydrogenii dioxidi is made according to the U. S. P. by adding to barium dioxide suspended in water of a temperature not above 10° C. (50° F.), diluted phosphoric acid until the reaction, which is first alkaline, has become neutral. Insoluble barium phosphate is formed, which is removed by filtration. From the clear filtrate traces of barium yet remaining in solution are precipitated by the addition of a few drops of sulphuric acid. The filtered solution is then diluted until it contains about 3 per cent., by weight, of pure dioxide, corresponding to about 10 volumes of available oxygen in 1 volume of the solution.

The solution is colorless and without odor, and has a slight acid reaction due to a trace of free sulphuric acid present; it is liable to deteriorate by age, especially on exposure to heat and light.

Glycozone is hydrogen dioxide dissolved in glycerin instead of in water.

Hydrogen dioxide may be recognized by the following reactions:

1. Silver oxide causes the decomposition of hydrogen dioxide with evolution of oxygen, metallic silver and water being formed at the same time:

$$Ag_2O + H_2O_2 = 2Ag + 2O + H_2O.$$

2. Mixed solutions of ferric chloride and potassium ferricyanide (which should have no blue tinge) assume an intense blue color on addition of even a very small quantity of hydrogen peroxide.

3. Solution of potassium permanganate, acidified with sulphuric acid, is readily decolorized with evolution of oxygen:

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = 8H_2O + 2MnSO_4 + K_2SO_4 + 10\ O.$$

This reaction is made use of in the volumetric analysis of hydrogen dioxide. (See Chapter 37.)

12. NITROGEN.

$N^{iii} = 14$ (14.01).

Occurrence in nature. By far the larger quantity of nitrogen is found in the atmosphere in a free state. Compounds containing nitrogen are chiefly the nitrates, ammonia, and many organic substances.

Preparation. Nitrogen is obtained usually from atmospheric air by the removal of its oxygen. This may be accomplished by burning a piece of phosphorus in a confined portion of air, when phosphoric oxide, a white solid substance, is formed, whilst nitrogen is left in an almost pure state.

Other methods for obtaining nitrogen are by heating a mixture of potassium nitrite and ammonium chloride dissolved in water:

$$\underset{\text{Potassium nitrite.}}{KNO_2} + \underset{\text{Ammonium chloride.}}{NH_4Cl} = KCl + 2H_2O + 2N;$$

or by heating ammonium nitrite in a glass retort:

$$NH_4NO_2 = 2H_2O + 2N.$$

Experiment 4. Use an apparatus as shown in Fig. 6, page 75. Place in the flask about 10 grammes of potassium nitrite and nearly the same amount of ammonium chloride; add enough water to dissolve the salts, and apply heat, which is to be carefully regulated from the time the decomposition begins, as the evolution of gas may otherwise become too rapid. Collect the gas, and notice its properties mentioned below.

QUESTIONS.—101. Mention two processes by which hydrogen may be obtained. 102. Show by symbols the decomposition of water by potassium, and of sulphuric acid by iron. 103. State the chemical and physical properties of hydrogen. 104. How many pounds of zinc are required to liberate 100 pounds of hydrogen? 105. State the composition of water in parts by weight and by volume. 106. Mention the most common solid and gaseous constituents of natural waters. 107. How does a mineral water differ from other waters? Mention some different kinds of mineral waters and their chief constituents. 108. What are the characteristics of a good drinking-water? 109. What are the purest natural waters, and by what process may chemically pure water be obtained? 110. State composition, mode of manufacture, and properties of hydrogen dioxide.

Properties. Nitrogen is a colorless, inodorous, tasteless gas; which, at a temperature of —130° C. (—202° F.) and a pressure of 280 atmospheres, may be condensed to a colorless liquid. It is neither, like oxygen, a supporter of combustion, nor, like hydrogen, a combustible substance; in fact, nitrogen is distinguished by having very little affinity for any other element, and it scarcely enters directly into combination with any substance. Nitrogen is not poisonous, yet not being a supporter of combustion it cannot sustain animal life. Nitrogen is trivalent in some compounds, quinquivalent in others.

4/5 - N

1/5 - O.

Atmospheric air is a mixture of about four-fifths of nitrogen and one-fifth of oxygen, with small quantities of aqueous vapor, carbon dioxide, and ammonia, containing frequently also traces of nitrous or nitric acid and occasionally hydrogen sulphide, sulphur dioxide, and hydro-carbons. Besides these gases there are always suspended in the air solid particles of dust and very minute cells of either animal or vegetable origin.

100 volumes of atmospheric air contain of

Oxygen	20.61	volumes.
Nitrogen	77.95	"
Carbon dioxide	0.04	"
Aqueous vapor	0.5–1.40	"
Ammonia Nitric acid	traces.	

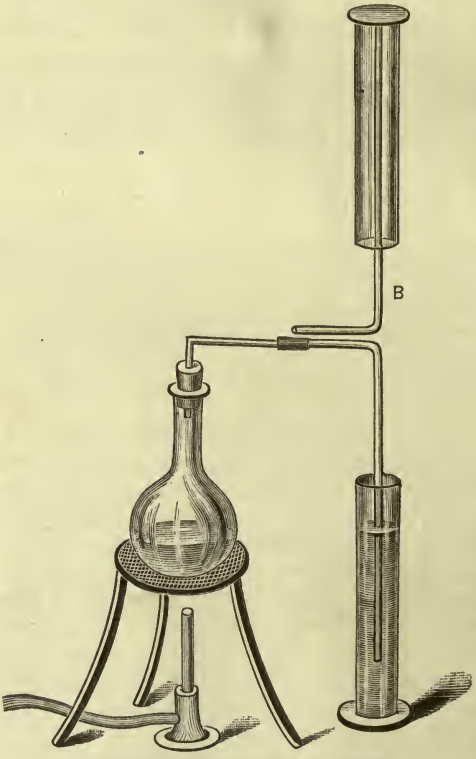
An analysis of air may be made by the following method: A graduated glass tube, containing a measured volume of air, is placed with the open end downward into a dish containing mercury. A small piece of phosphorus is then introduced and allowed to remain in contact with the air for several hours, when it gradually combines with the oxygen. The remaining volume of air is chiefly nitrogen, the loss in volume represents oxygen.

For the determination of carbon dioxide and water, a measured volume of air is passed through two U-shaped glass tubes. One of these tubes has previously been filled with pieces of calcium chloride, the other tube with pieces of potassium hydroxide, and both tubes have been weighed separately. In passing the measured air through these tubes the first one will retain all the moisture, the second one all the carbon dioxide; the increase in weight of the tubes at the end of the operation will give the amounts of the two constituents.

That oxygen is found in the atmosphere in a free state is explained by the fact that all elements having affinity for oxygen have entered into combination with it, whilst the excess is left uncombined. Nitrogen is found uncombined, because it has so little affinity for other elements.

Ammonia, $NH_3 = 17$. This compound is constantly forming in nature by the decomposition of organic (chiefly animal) matter, such as meat, urine, blood, etc. It is also obtained during the process of destructive distillation, which is the heating of non-volatile organic substances in suitable vessels to such an extent that decomposition takes place, the generated volatile products being collected in receivers. The manufacture of illuminating gas is such a process of destructive distillation; coal is heated in retorts, and most of the nitrogen contained in the coal is converted into and liberated as ammonia gas, which is absorbed in water, through which the gas is made to pass.

Fig. 8.



Apparatus for generating ammonia.

Another method of obtaining ammonia is through decomposition of ammonium salts by the hydroxides of sodium, potassium, or calcium. Usually ammonium chloride is mixed with calcium hydroxide and heated, when calcium chloride, water, and ammonia are formed:

$$2(NH_4Cl) + Ca(OH)_2 = CaCl_2 + 2H_2O + 2NH_3.$$

Experiment 5. Mix about equal weights (10 grammes of each) of ammonium chloride and calcium hydroxide (slaked lime) in a flask of about 200 c.c. capacity, and arranged as in Fig. 8; cover the mixture with water and apply heat. As long as any atmospheric air remains in the apparatus, bubbles of it will pass through the water contained in the cylinder; afterward all gas will be readily and completely absorbed by the water. Notice the odor and alkaline reaction on litmus of the ammonia water thus obtained. When the gas is being freely liberated, move the tube upward, as shown in B, and collect the gas by upward displacement in a cylinder or tube, which when filled with gas is held mouth downward into water, which will rapidly rise in the tube by absorption of the gas. Notice that ammonia is not readily combustible, by applying a flame to the gas escaping from the delivery tube.

Ammonia is a colorless gas, of a very pungent odor, an alkaline taste, and a strong alkaline reaction. In pure oxygen it burns, forming water and free nitrogen.

By the mere application of a pressure of seven atmospheres or by intense cold (—40° C., —40° F.), ammonia may be converted into a liquid, which at —80° C. (—112° F.) forms a solid crystalline mass. Water dissolves about 700 times its volume of ammonia gas, forming ammonium hydroxide:

$$NH_3 + H_2O = NH_4OH.$$

For analytical reactions of ammonia, see Ammonium compounds.

Water of ammonia, Aqua ammoniæ (*Spirit of hartshorn*). This is a solution of ammonia gas in water or *ammonium hydroxide* in water. The common water of ammonia contains 10 per cent. by weight of ammonia, and has a specific gravity of 0.96; the *stronger water of ammonia, aqua ammoniæ fortior*, contains 28 per cent., and has a specific gravity of 0.901. Ammonia water has the odor, taste, and reaction which characterize the gas.

Compounds of nitrogen and oxygen. Five distinct compounds of nitrogen and oxygen are known. They are named and constituted as follows:

	Composition.			
	By weight.		By volume.	
	N	O	N	O
Nitrogen monoxide, N_2O	28	16	2	1
Nitrogen dioxide, $N_2O_2 = 2(NO)$	28	32	2	2
Nitrogen trioxide, N_2O_3	28	48	2	3
Nitrogen tetroxide, $N_2O_4 = 2(NO_2)$	28	64	2	4
Nitrogen pentoxide, N_2O_5	28	80	2	5

The first, third, and fifth of these compounds are capable of combining with water to form acids, known as hyponitrous, nitrous, and nitric acid, respectively.

The gaseous compounds N_2O_2 and N_2O_4 exist as such at low temperatures only, and readily split up at a high temperature into the compounds NO and NO_2. This splitting up of molecules is known as *dissociation.* The terms nitrogen dioxide and nitrogen tetroxide should be applied only to the compounds N_2O_2 and N_2O_4, but they are used also for the products of dissociation NO and NO_2.

When electric sparks pass through atmospheric air some ozone is generated which oxidizes nitrogen, forming first the lower and then also the higher oxides; these combine with water to form nitrous and nitric acid, which acids are taken up by the ammonia present in the air, forming the respective ammonium salts.

Nitrogen monoxide, $N_2O=44$. (Sometimes called *nitrous oxide;* also *laughing gas*). This compound was discovered by Priestley in 1776; its anæsthetic properties were first noticed in 1800 by Sir Humphrey Davy, and it was first used in dentistry by Dr. Howard Wells, a dentist of Hartford, Conn., in 1844. It may be easily obtained by heating ammonium nitrate in a flask at a temperature not exceeding 250° C. (482° F.), when the salt is decomposed into nitrogen monoxide and water:

$$NH_4NO_3 = 2H_2O + N_2O.$$

When nitrous oxide is prepared for use as an anæsthetic it should be passed through two wash-bottles containing caustic soda and ferrous sulphate respectively; these agents will retain any impurities that may be formed during the decomposition, especially from an impure salt.

Experiment 6. Use apparatus as represented in Fig. 6, page 75. Place in the dry flask about 10 grammes of ammonium nitrate, apply heat, collect the gas in cylinders over water, and verify by experiments and observations the correctness of the statements below regarding the physical and chemical properties of nitrogen monoxide.

Nitrogen monoxide is a colorless, almost inodorous gas, of distinctly sweet taste. It supports combustion almost as energetically as oxygen, but differs from this element by its solubility in cold water, which absorbs nearly its own volume. Under a pressure of about 50 atmospheres it condenses to a colorless liquid, the boiling-point of which is at about —80° C. (—112° F.) and the freezing-point at —100° C. (—148° F.)

When inhaled it causes exhilaration, intoxication, anæsthesia, and finally asphyxia. The gas is used in dentistry as an anæsthetic, the liquefied compound being sold for this purpose in wrought-iron cylinders.

Nitrogen dioxide, $NO=30$. This is a colorless gas which is formed generally when nitric acid acts upon metals or upon substances which deoxidize it. It is capable of combining directly with one or more atoms of oxygen, thereby forming NO_2, *nitrogen tetroxide,* which is a gas of deep red color and poisonous properties. *Nitrogen trioxide* is of no practical interest.

Experiment 7. Pour about 1 c.c. of nitric acid upon a few fragments of metallic copper, and apply heat. Notice that red fumes escape, which are nitrogen tetroxide, and that a blue solution is formed which contains cupric nitrate. See explanation of the change below.

Hyponitrous acid, HNO, and nitrous acid, HNO_2, have not been isolated and are known in combination only. Nitrous acid and nitrites occur, in small quantity, in air, and also in water, where they are formed by decomposition of nitrogenous organic matter.

Nitrites evolve red fumes on the addition of sulphuric acid; they act as reducing agents decolorizing acidified solution of potassium permanganate; they color blue a mixture of zinc iodide and starch solution; they give a dark-brown color with solution of meta-phenylene-diamine, $C_6H_4(NH_2)_2$, in the presence of free sulphuric acid.

Nitric acid, Acidum nitricum, HNO_3=63 (*Aqua fortis, Hydric nitrate*). Nitrogen pentoxide, N_2O_5, a white, solid, unstable compound, is of scientific interest only. When brought in contact with water it readily combines with it, forming nitric acid:

$$N_2O_5 + H_2O = 2HNO_3.$$

The usual method for obtaining nitric acid is the decomposition of sodium nitrate by sulphuric acid:

$$NaNO_3 + H_2SO_4 = HNO_3 + \underset{\text{Sodium bisulphate.}}{HNaSO_4};$$

or

$$2NaNO_3 + H_2SO_4 = 2HNO_3 + \underset{\text{Sodium sulphate.}}{Na_2SO_4}.$$

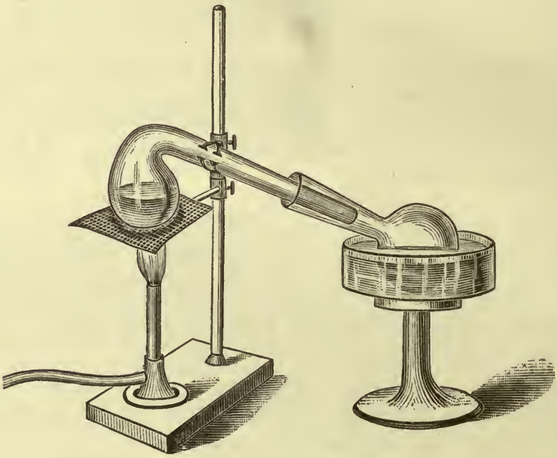
Experiment 8. Prepare an apparatus as shown in Fig. 9. Heat in a retort of about 250 c.c. capacity a mixture of about 50 grammes of potassium nitrate and nearly the same weight of sulphuric acid. Nitric acid is evolved and distils over into the receiver, which is to be kept cool during the operation by pouring cold water upon it or by surrounding it with pieces of ice. Examine the properties of nitric acid thus made, and use it for the tests mentioned below. How much pure nitric acid can be obtained from 50 grammes of potassium nitrate? Weigh the acid which you obtain in the experiment and compare this weight with the theoretical quantity.

The acid thus obtained is an almost colorless, fuming, corrosive liquid, of a peculiar, somewhat suffocating odor, and a strongly acid reaction. When exposed to sunlight it assumes a yellow or yellowish-red color in consequence of its decomposition into nitrogen tetroxide, water, and oxygen.

Common nitric acid, of a specific gravity 1.414, is composed of 68 per cent. of HNO_3 and 32 per cent. of water. The *diluted nitric acid* of the U. S. P. is made by mixing ten parts by weight of the common acid with fifty-eight parts of water, and contains 10 per cent. of absolute nitric acid; it has a specific gravity of 1.057.

Fuming nitric acid has a brown-red color, due to nitrogen tetroxide, and emits vapors of the same color. Specific gravity 1.45 to 1.50.

FIG. 9.



Distillation of nitric acid.

Nitric acid is completely volatilized by heat; it stains animal matter distinctly yellow; it is a monobasic acid forming salts called nitrates. These salts are all soluble in water, for which reason nitric acid cannot be precipitated by any reagent. Nitric acid is a strong oxidizing agent; this means that it is capable of giving off part of its oxygen to substances having affinity for it.

The action of nitric acid upon such metals as copper, silver, and many others involves two changes, viz.: displacement of the hydrogen of the acid by the metal:

$$Cu + 2HNO_3 = Cu(NO_3)_2 + 2H;$$

and the deoxidation of another portion of nitric acid by the liberated hydrogen while yet in the nascent state. Thus:

$$HNO_3 + 3H = 2H_2O + NO.$$

The liberated nitrogen dioxide, which is colorless, readily absorbs oxygen from the air, forming red vapors of nitrogen tetroxide.

Tests for nitric acid or nitrates.

(Potassium nitrate, KNO_3, may be used as a nitrate.)

1. Nitric acid when heated with copper filings, or nitrates when heated with copper filings and sulphuric acid, evolve red fumes of nitrogen tetroxide. (See explanation above.) On the addition of alcohol to the mixture, the odor of nitrous ether is noticed.

2. The solution of a nitrate, to which a few small pieces of ferrous sulphate have been added, will show a reddish-purple or black coloration upon pouring a few drops of strong sulphuric acid down the side of the test-tube, so that it may form a layer at the bottom of the tube. The black color is due to the formation of an unstable compound of the composition $2FeSO_4.NO$.

3. Solution of indigo is changed to yellow by nitric acid. Solutions of nitrates mixed with dilute sulphuric acid do not bleach indigo in the cold, but do so on heating.

4. Nitrates deflagrate when heated on charcoal by means of the blowpipe.

5. When a few drops of a solution of 1 part of brucine in 300 parts of 5 per cent. dilute sulphuric acid are added to a very dilute solution of a nitrate, and then some concentrated sulphuric acid is carefully poured down the side of the test-tube, a red color, changing to yellow, is produced at the line of contact.

6. When a few drops of solution of diphenylamine, $NH(C_6H_5)_2$, in concentrated sulphuric acid are added to solution of a nitrate, and then concentrated sulphuric acid is poured down the side of the test-tube, a deep-blue color is formed at the line of contact.

7. Crystals of pyrogallic acid, $C_6H_3(OH)_3$, added to solution of a nitrate, and then concentrated sulphuric acid poured down the side of the test-tube, produce a deep-brown color at the line of contact.

Reactions 5, 6, and 7 show 1 part of nitric acid in one, three, and ten million parts of water respectively, and are used chiefly to detect traces of nitric acid in drinking-water. As sulphuric acid may contain nitric acid, the tests should also be made with the sulphuric acid alone in order to prove its purity.

As an antidote in cases of poisoning by nitric acid a solution of sodium carbonate, or a mixture of magnesia and water, may be administered with the view of neutralizing the acid.

QUESTIONS.—111. State the physical and chemical properties of nitrogen. 112. Mention the principal constituents of atmospheric air and the quantity in which they are present. 113. By what processes can the four chief constituents

13. CARBON.

$C^{iv} = 12 (11.97)$.

Occurrence in nature. Carbon is a constituent of all organic matter. In a pure state it is found crystallized as diamond and graphite, amorphous in a more or less pure condition in the various kinds of coal, charcoal, boneblack, lampblack, etc. As carbon dioxide, carbon is found in the air; as carbonic acid, in water; as carbonates (marble, limestone, etc.), in the solid portion of our earth.

Properties. The three different allotropic modifications of carbon differ widely from each other in their physical properties.

Diamond is the purest form of carbon, in which it is crystallized in regular octahedrons, cubes, or in some figure geometrically connected with these. Diamond is the hardest substance known; it is infusible, but burns when heated intensely, forming carbon dioxide.

Graphite, plumbago, or *black-lead,* is carbon crystallized in short six-sided prisms; it is a somewhat rare, dark-gray mineral, chiefly used for lead-pencils.

Amorphous carbon is a soft, black, solid substance.

Neither form of carbon is fusible, volatile, or soluble in any of the common solvents.

Carbon is a quadrivalent element; it has little affinity for metals, but combines with many of the non-metals. chiefly with oxygen, hydrogen, and nitrogen, forming organic substances.

Tests for carbon.

1. Most non-volatile (organic) substances containing carbon, blacken when heated on platinum foil. Starch or sugar may be used for this test.

2. The product of combustion of carbon (or of combustible matter containing it), CO_2, renders lime-water turbid, in consequence of the formation of insoluble calcium carbonate, $CaCO_3$.

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of atmospheric air be determined? 114. Mention some decompositions by which ammonia is generated. 115. Explain the process of making water of ammonia. 116. State the physical and chemical properties of ammonia gas and ammonia water. 117. How is nitrogen monoxide obtained, and what are its properties? 118. Describe the process for making nitric acid, and give symbols for decomposition. 119. How does nitric acid act on animal matter, and what are its properties generally? 120. Give tests and antidote for nitric acid.

Carbon dioxide, $CO_2 = 44$. (Formerly named *carbonic acid*, or *anhydrous carbonic acid.*) This compound is always formed during the combustion of carbon or of organic matter ; also during the decay (slow combustion), fermentation, and putrefaction (processes of decomposition) of organic matter ; it is constantly produced in the animal system, exhaled from the lungs, and given off through the skin. Many spring waters contain considerable quantities of the gas, one single spring in Nauheim, Germany, liberating as much as 3000 pounds of carbon dioxide a day.

By heating, many carbonates are decomposed into oxides of the metals and carbon dioxide.

Lime-burning is such a process of decomposition :

$$\underset{\text{Calcium carbonate.}}{CaCO_3} = \underset{\text{Calcium oxide.}}{CaO} + CO_2.$$

Another method for the generation of carbon dioxide is the decomposition of any carbonate by an acid :

$$\underset{\text{Calcium carbonate.}}{CaCO_3} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Calcium chloride.}}{CaCl_2} + H_2O + CO_2.$$

Experiment 9. Use apparatus represented in Fig. 7, page 79. Place about 20 grammes of marble, $CaCo_3$, in small pieces (sodium carbonate or any other carbonate may be used) in the flask, cover it with water, and add hydrochloric acid through the funnel-tube. The escaping gas may be collected over water, as in the case of hydrogen, or by downward displacement, *i. e.*, by passing the delivery-tube to the bottom of a tube or other suitable vessel, when the carbon dioxide, on account of its being heavier than atmospheric air, gradually displaces the latter. This will be shown by examining the contents of the vessel with a burning paper, which is extinguished as soon as most of the air has been expelled.

Examine the gas for its high specific gravity, by pouring it from one vessel into another; for its power of extinguishing flames, by mixing it with an equal volume of air, which mixture will be found not to support the combustion of a taper notwithstanding that oxygen is contained in it. Add to one portion of the collected gas some lime-water, shake it, and notice that it becomes turbid. Blow air exhaled from the lungs through a glass tube into lime-water, and notice that it also turns turbid.

Carbon dioxide is a colorless, odorless gas, having a faintly acid taste. By a pressure of 38 atmospheres, at a temperature of 0° C. (32° F.), carbon dioxide is converted into a colorless liquid, which by intense cold (—79° C., —110° F.) may be converted into a white, solid, crystalline, snow-like substance. The specific gravity of carbon dioxide is 1.524; it is consequently about one-half heavier than atmospheric air.

Cold water absorbs at the ordinary pressure about its own volume of carbon dioxide, and much larger quantities under an increased pressure (soda water).

Carbon dioxide is not combustible, and not a supporter of combustion; on the contrary, it has a decided tendency to extinguish flames, air containing one-tenth of its volume of carbon dioxide being unable to support the combustion of a candle. Whilst not poisonous when taken into the stomach, carbon dioxide acts indirectly as a poison when inhaled, because it cannot support respiration, and prevents, moreover, the proper exchange between the carbon dioxide of the blood and the oxygen of the atmospheric air.

Common atmospheric air contains about 4 volumes of carbon dioxide in 10,000 of air, or 0.04 per cent. In the process of respiration this air is inhaled, and a portion of the oxygen is absorbed in the lungs by the blood, which conveys it to the different portions of the animal body, and receives in exchange for the oxygen a quantity of carbon dioxide, produced by the union of a former supply of oxygen with the carbon of the different organs to which the blood is supplied. The air issuing from the lungs contains this carbon dioxide, in quantity about 4 volumes in 100 of exhaled air, which is 100 times more than contained in fresh air.

Exhaled air is, moreover, contaminated by other substances than carbon dioxide, such as ammonia, hydrocarbons, and most likely traces of other organic bodies, the true nature of which has not been fully recognized, but which seem to be directly poisonous. The bad effects experienced in breathing air which has become contaminated by the exhalations from the lungs, are most likely due to these unknown bodies. As we have as yet no methods of ascertaining the quantity of these poisonous substances present in exhaled air, the determination of the amount of exhaled carbon dioxide present must serve as an indicator of the fitness of an air for breathing purposes. As a general rule, it may be stated that it is not advisable to breathe, for any length of time, air containing more than 0.1 per cent. of exhaled carbon dioxide; in air containing 0.5 per cent. most persons are attacked by headache, still larger quantities produce insensibility, and air containing 8 per cent. of carbon dioxide causes death in a few minutes.

As exhaled air contains from 3.5 to 4 per cent. of carbon dioxide, it is unfit to be breathed again. The total amount of carbon dioxide evolved by the lungs and skin of a grown person amounts to about 0.7 cubic foot per hour. Hence the necessity for a constant supply of fresh air by ventilation. This becomes the more necessary where an additional quantity of carbon dioxide is supplied by illuminating flames.

Mentioned above are many processes by which carbon dioxide is constantly produced in nature, and we might assume that the amount of 0.04 per cent. of carbon dioxide contained in atmospheric air would gradually increase. This, however, is not the case, because plants, and more especially all their green parts, are capable of absorbing carbon dioxide from the air, whilst at the same time they liberate oxygen.

This process of vegetable respiration (if we may so call it), which takes place under the influence of sunlight, is, consequently, the reverse of that of animal respiration. The animal uses oxygen and liberates carbon dioxide; the plant consumes this carbon dioxide and liberates oxygen.

Carbon dioxide is an acid oxide, which combines with water, forming carbonic acid:

$$CO_2 + H_2O = H_2CO_3.$$

Carbonic acid, H_2CO_3, is not known in a pure state, but always diluted with much water, as in all the different natural waters. Carbonic acid is a bibasic, extremely weak acid, the salts of which are known as carbonates. Many of these carbonates (calcium carbonate, for instance) are abundantly found in nature.

Tests for carbon dioxide, carbonic acid, and carbonates.

(Sodium carbonate, Na_2CO_3, may be used)

1. Pass carbon dioxide through lime-water, which is rendered turbid by the formation of calcium carbonate:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

2. From carbonates, evolve the gas by the addition of some acid, and examine it by the same method.

3. The soluble carbonates of potassium, sodium, and ammonium, give precipitates with the solutions of most metallic salts; for instance, with the chlorides of Ba, Ca, Sr, Mg, Fe, Zn, Cu, etc.

Carbon monoxide, carbonic oxide, $CO = 28$. Carbon monoxide is a colorless, odorless, tasteless, neutral gas, almost insoluble in water; it burns with a pale-blue flame, forming carbon dioxide; it is very poisonous when inhaled, forming with the coloring matter of the blood a compound which prevents the absorption of oxygen. Carbon monoxide is formed when carbon dioxide is passed over red-hot coal.

$$CO_2 + C = 2CO.$$

The conditions necessary for the formation of carbon monoxide are, consequently, present in any stove or furnace where coal burns with an insufficient supply of air. The carbon dioxide formed in the lower parts of the furnace is decomposed by the coal above. The blue flames frequently playing over a coal fire are burning carbon monoxide. This gas is formed also by the decomposition of oxalic acid (and many other organic substances) by sulphuric acid:

$$\underset{\text{Oxalic acid.}}{H_2C_2O_4} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = H_2SO_4.H_2O + CO_2 + CO.$$

Carbon monoxide is now manufactured on a large scale by causing the decomposition of steam by coal heated to red heat. The decomposition takes place thus:

$$H_2O + C = 2H + CO.$$

The gas mixture, thus obtained and known as *water-gas*, may be used for heating purposes directly, but has to be mixed with hydrocarbons when used as an illuminating agent, for reasons which will be pointed out below when considering the nature of flames.

Compounds of carbon and hydrogen. There are no other two elements which are capable of forming so large a number of different combinations as are carbon and hydrogen. Several hundred of these hydrocarbons are known, and their consideration belongs to the domain of organic chemistry.

Two of these hydrocarbons, however, may be briefly mentioned, as they are of importance in the consideration of common flames. These compounds are: *methane* (marsh-gas, fire-damp), CH_4; and *ethene* (olefiant gas), C_2H_4.

Both compounds are colorless, almost odorless gases, and both are products of the destructive distillation of organic substances. Destructive distillation is the heating of non-volatile organic substances in such a manner that the oxygen of the atmospheric air has no access, and to such an extent that the molecules of the organic matter are split up into simpler compounds. Among the gaseous products formed by this operation, more or less of the two hydrocarbons mentioned above is found.

Marsh-gas is formed frequently by the decomposition of organic matter in the presence of moisture (leaves, etc., in swamps); and during the formation of coal in the interior of the earth the gas often gives rise to explosion in coal mines. During these explosions of the methane (mixed with air and other gases), called *fire-damp* by the miners, carbon is converted into carbon dioxide, which the miners speak of as *choke-damp*, or *after-damp*.

Flame is gas in the act of combustion. Of combustible gases, have been mentioned: hydrogen, carbon monoxide, marsh-gas, and olefiant gas. These four gases are actually those which are found chiefly in any of the common flames produced by the combustion of organic matter, such as paper, wood, oil, wax, or illuminating gas itself.

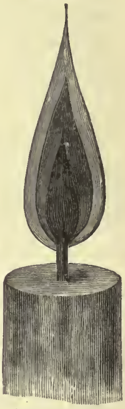
These gases are generated by destructive distillation, the heat being supplied either by a separate process (manufacture of illuminating gas by heating wood or coal in retorts), or generated during the combustion itself.

In burning a candle, for instance, fat is constantly decomposed by the heat of the flame itself, the generated gases burning continuously until all fat has been decomposed, and the products of decomposition have been burned up, *i. e.*, have been converted into carbon dioxide and water.

An ordinary flame (Fig. 10) consists of three parts or cones. The inner or central portion is chiefly unburnt gas; the second is formed of partially burnt and burning gas; the outer cone, showing the highest temperature, but scarcely any light, is that part of the flame where complete combustion takes place.

The light of a flame is caused by solid particles of carbon heated to a white heat. The separation of carbon in the flame is explained by the fact that hydrogen has a greater affinity for oxygen than has carbon; only a limited amount of oxygen can penetrate into the flame, and the hydrogen of the hydrocarbon will consume this oxygen, the carbon being liberated momentarily until it reaches the outer cone, where it finds sufficient oxygen with which to combine.

FIG. 10.



Structure of flame.

If a sufficient amount of air be previously mixed with the illuminating gas, as is done in the *Bunsen burner*, no separation of carbon takes place, and, therefore, no light is produced, but a more intense heat is generated.

Silicon or Silicium, Si = 28.3, is found in nature very abundantly as silicon dioxide, or silica, SiO_2 (rock-crystal, quartz, agate, sand), and in the form of silicates, which are silicic acid in which the hydrogen has been replaced by metals. Most of our common rocks, such as granite, porphyry, basalt, feldspar, mica, etc., are such silicates, or a mixture of them. Small quantities of silica are found in spring waters, as well as in vegetable and animal bodies.

Silicon resembles carbon both in its physical and chemical properties. Like carbon, it is known in the amorphous state, and forms two kinds of crystals, which resemble graphite and diamond. Like carbon, silicon is quadrivalent, forming silicon dioxide, SiO_2, silicic acid, H_2SiO_3, silicon hydride, SiH_4, silicon chloride, $SiCl_4$, which compounds are analogous to the corresponding carbon compounds, CO_2, H_2CO_3, CH_4, and CCl_4.

The compounds formed by the union of silicon with hydrogen, chlorine, and fluorine are gases. The latter compound, silicon fluoride, SiF_4, is obtained by the action of hydrofluoric acid on silica or silicates, thus:

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

This reaction is used in the analysis of silicates, which are decomposed and rendered soluble by the action of hydrofluoric acid.

Silicon fluoride is decomposed by water into silicic acid and hydrofluosilicic acid, H_2SiF_6, thus:

$$3SiF_4 + 3H_2O = H_2SiO_3 + 2H_2SiF_6.$$

Several varieties of silicic acid are known, of which may be mentioned the *normal silicic acid*, H_4SiO_4, and the *ordinary silicic acid*, H_2SiO_3, from the latter of which, by heating, water may be expelled, when *silicon dioxide*, SiO_2, is left.

Tests for silicic acid and silicates.

(Soluble glass or flint may be used.)

1. Silicic acid and most silicates are insoluble in water and acids. By fusing silicates with about 5 parts of a mixture of the carbonates of sodium and potassium, the silicates of these metals (known as soluble glass) are formed. By dissolving this salt in water and acidifying the solution with hydrochloric acid a portion of the silica separates as the gelatinous hydroxide. Complete separation of the silica is accomplished by evaporating the mixture to complete dryness over a water-bath, and re-dissolving the chlorides of the metals in water acidulated with hydrochloric acid; silica remains undissolved as a white, amorphous powder.

2. Silica or silicates when added to a bead of microcosmic salt (see index) form on heating before the blowpipe the so-called silica-skeleton.

Boron, $B''' = 10.9$, is found in but few localities, either as boric (boracic) acid or sodium borate (borax). Formerly the total supply of boron was derived from Italy; large quantities of borax are now obtained from Nevada.

Boric acid, Acidum boricum, $H_3BO_3 = 61.9$ (*Boracic acid*), is a white, crystalline substance, which is sparingly soluble in cold water, somewhat more soluble in alcohol and in glycerin; it has but weak acid properties. When heated to 100° C. (212° F.) it loses water, and is converted into *metaboric acid,* HBO_2, which when heated yet higher is converted into *tetraboric acid,* $H_2B_4O_7$, from which *borax,* $Na_2B_4O_7 + 10H_2O$, is derived. At a white heat boric acid loses all water, and is converted into boron trioxide, B_2O_3

Boric acid is obtained by adding hydrochloric acid to a hot saturated solution of borax, when boric acid separates on cooling. The chemical change is this:

$$Na_2B_4O_7 + 2HCl + 5H_2O = 4H_3BO_3 + 2NaCl.$$

Tests for boric acid and borates.

(Sodium borate, $Na_2B_4O_7 \cdot 10H_2O$, may be used.

1. Heat some borax on the loop of a platinum wire. Notice that it swells up during the time that water is expelled, and then melts into a transparent, colorless bead of fused borax.

2. To a concentrated neutral solution of a borate add solution of either calcium, barium, or silver. In either case white precipitates of borates are formed, having the composition CaB_4O_7, BaB_4O_7, or $Ag_2B_4O_7$.

3. Mix in a porcelain dish some borax with a few drops of sulphuric acid, pour upon the mixture some alcohol and ignite. The flame has a seam or mantle of a green color, which is best seen by repeatedly extinguishing and rekindling the alcohol. A borax bead moistened with sulphuric acid and heated in a flame also colors it green.

4. To a warm saturated solution of a borate add some hydrochloric or sulphuric acid. On cooling, shining scales of boric acid separate.

5. A solution of borax, even when acidulated with hydrochloric acid, colors turmeric-paper brown, after this has been dried.

QUESTIONS.—121. How is carbon found in nature? 122. State the physical and chemical properties of carbon in its three allotropic modifications. 123. Mention three different processes by which carbon dioxide is generated in nature, and some processes by which it is generated by artificial means. 124. State the physical and chemical properties of carbon dioxide. 125. Explain the process of respiration from a chemical point of view. 126. What is the percentage of carbon dioxide in atmospheric air, and why does its amount not increase? 127. State the composition of carbonic acid and of a carbonate. How can they be recognized by analytical methods? 128. Under what circumstances will carbon monoxide form, and how does it act when inhaled? 129. What is destructive distillation, and what gases are generally formed during that process? 130. Explain the structure and luminosity of flames.

14. SULPHUR.

$S^{ii} = 32$ (31.97).

Occurrence in nature. Sulphur is found in the uncombined state in volcanic districts, the chief supply being derived from Sicily. In combination sulphur is widely diffused in the form of sulphates (gypsum, $CaSO_4.2H_2O$), and frequently as sulphides (iron pyrites, FeS_2, galena, PbS, cinnabar, HgS, etc.). Sulphur enters also into organic compounds, during the decomposition of which sulphur is evolved as hydrogen sulphide, which gas is also a constituent of some waters.

Properties. Sulphur is a yellow, brittle, solid substance, having neither taste nor odor. It is insoluble in water and nearly so in alcohol; soluble in benzene, benzin, ether, chloroform, carbon disulphide, oil of turpentine, and fat oils. Sulphur is polymorphous; it crystallizes, from a solution in disulphide of carbon, in octahedrons with a rhombic base; when, however, liquefied by heat it crystallizes in six-sided prisms, and is obtained as a brown, amorphous substance by pouring melted sulphur into cold water.

Sulphur melts at 115° C. (239° F.) to an amber-colored liquid, which is fluid as water; increasing the heat gradually, it becomes brown and thick, and at about 200° C. (392° F.) it is so tenacious that it scarcely flows; when heated still further the sulphur again becomes thin and liquid, and, finally, boils at a temperature of about 440° C. (824° F.).

In its chemical properties sulphur resembles oxygen, being like this element bivalent, and supporting, when in the form of vapor, the combustion of many substances, especially of metals. Many compounds of oxygen and sulphur show an analogous composition, as for instance H_2O and H_2S, CO_2 and CS_2, CuO and CuS.

Crude sulphur is that obtained from the localities where it is found. It contains generally from 2 to 4 per cent. of earthy impurities. Melted sulphur poured into round moulds is known as *roll-sulphur* or *brimstone.*

Sublimed sulphur, Sulphur sublimatum (*Flowers of sulphur*). Obtained by heating sulphur to the boiling-point in suitable vessels, and passing the vapor into large chambers, where it deposits in the form of a powder, composed of small crystals.

Washed sulphur, Sulphur lotum, is sublimed sulphur washed with a very dilute ammonia water, and then with pure water; the object of this treatment being to free the sulphur from all adhering sulphurous and sulphuric acid, as also from arsenic compounds which are sometimes present.

Precipitated sulphur, Sulphur præcipitatum (*Milk of sulphur*). Made by boiling one part of calcium hydroxide with two parts of sulphur and thirty parts of water, filtering the solution, adding to it dilute hydrochloric acid until nearly neutral, washing and drying the precipitated sulphur.

By the action of sulphur on calcium hydroxide are formed calcium polysulphide, calcium hyposulphite, and water:

$$\underset{\text{Calcium hydroxide.}}{3(Ca2OH)} + \underset{\text{Sulphur.}}{12S} = \underset{\text{Calcium Polysulphide.}}{2CaS_5} + \underset{\text{Calcium Hyposulphite.}}{CaS_2O_3} + \underset{\text{Water.}}{3H_2O}.$$

On adding hydrochloric acid to the solution, both substances are decomposed and sulphur is liberated:

$$2CaS_5 + CaS_2O_3 + 6HCl = 3CaCl_2 + 3H_2O + 12S.$$

Precipitated sulphur differs from sublimed sulphur by being in a more finely divided state, and by having a much paler yellow, almost white color.

Sulphur dioxide, $SO_2 = 64$ (*Sulphurous anhydride,* improperly also called *sulphurous acid*).

Two combinations of sulphur and oxygen are known; they are sulphur dioxide, SO_2, and sulphur trioxide, SO_3.

Sulphur dioxide is formed always when sulphur or substances containing it in a combustible form (H_2S, CS_2, etc.) burn in air. It is formed also by the action of strong sulphuric acid on many metals (Cu, Hg, Ag, etc.), or on charcoal:

$$\underset{\text{Sulphuric acid.}}{2H_2SO_4} + \underset{\text{Copper.}}{Cu} = \underset{\text{Cupric sulphate.}}{CuSO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Sulphur dioxide.}}{SO_2}.$$

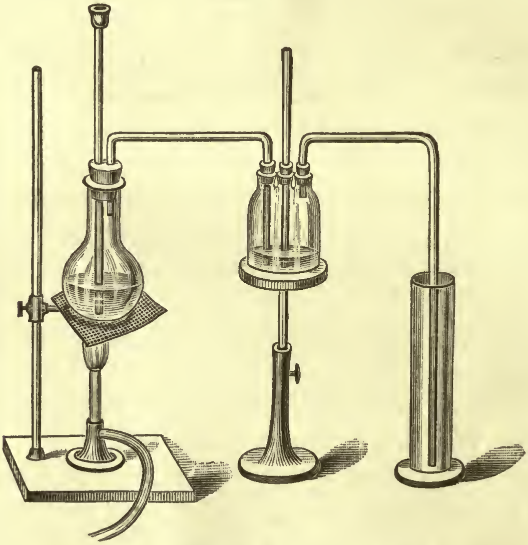
$$2H_2SO_4 + C = CO_2 + 2H_2O + 2SO_2.$$

Sulphur dioxide is a colorless gas, having a suffocating, disagreeable odor; it liquefies at a temperature of —10° C. (14° F.), and solidifies at —60° C. (—76° F.); it is very soluble in water, forming sulphurous acid; it is a strong, deoxidizing, bleaching, and disinfecting agent; when inhaled in a pure state it is poisonous; when diluted with air it produces coughing and irritation of the air-passages.

Sulphurous acid, Acidum sulphurosum, $H_2SO_3 = 82$. One volume of cold water absorbs about 40 volumes of sulphur dioxide, equal to about 11 per cent. by weight. The official acid must contain not less than 6.4 per cent. by weight, equal to about 2250 volumes of gas dissolved in 100 of water. According to the U. S. P. the acid is made by generating sulphur dioxide from charcoal and sulphuric acid in a flask, and passing the gas through a wash-bottle containing water, into distilled water for absorption.

Experiment 10. Use an apparatus as shown in Fig. 11. Place in the flask about 20 grammes of charcoal in small pieces, cover it with sulphuric acid, apply heat, and pass the generated gas first through a small quantity of water contained in the wash-bottle, and then into pure water, contained in the cylinder.

FIG. 11.



Apparatus for making sulphurous acid.

The solution, sulphurous acid, may be used for the tests mentioned below; when the neutral solution of a sulphite is required, make this by adding solution of sodium carbonate to a portion of the sulphurous acid until litmus-paper shows neutral reaction. Examine also the contents of the wash-bottle by means of the tests given below for sulphuric acid; most likely some of the latter will be found. How much carbon and how much H_2SO_4 are required to make 100 grammes of a 6.4 per cent. sulphurous acid?

Thus obtained, sulphurous acid is a colorless acid liquid, which has the odor as well as the disinfecting and bleaching properties of sulphur dioxide; it is completely volatilized by heat. Sulphurous acid is a dibasic acid, the salts of which are termed *sulphites*.

Tests for sulphurous acid and sulphites.

(Sodium sulphite, Na_2SO_3, may be used.)

1. Sulphurous acid, or the gaseous sulphur dioxide liberated from sulphites by the addition of sulphuric acid, decolorizes an acidified solution of potassium permanganate, in consequence of the deoxidation of the latter.

2. Similarly to the above, an acid solution of potassium dichromate is turned green by conversion of chromic acid into chromic oxide.

3. When sulphurous acid or sulphites are added to diluted sulphuric acid and zinc (which evolve hydrogen), hydrogen sulphide is liberated.

$$H_2SO_3 + 6H = H_2S + 3H_2O.$$

4. Barium chloride added to a neutral solution of a sulphite produces a white precipitate of barium sulphite, soluble in diluted hydrochloric acid; barium sulphate is insoluble in hydrochloric acid.

$$Na_2SO_3 + BaCl_2 = BaSO_3 + 2NaCl.$$

Sodium sulphite.	Barium chloride.	Barium sulphite.	Sodium chloride.

5. Silver nitrate produces a white precipitate of silver sulphite, which darkens when heated, metallic silver and sulphuric acid being formed:

$$Ag_2SO_3 + H_2O = 2Ag + H_2SO_4.$$

6. A strip of paper, moistened with mercurous nitrate solution, turns black when suspended in sulphur dioxide.

Sulphur trioxide, $SO_3 = 80$ (*Anhydrous sulphuric acid*). This is a white, silk-like solid substance, having a powerful affinity for water; it may be obtained by the action of phosphoric oxide on strong sulphuric acid, or by passing sulphur dioxide and oxygen together over heated platinum-sponge; it is of scientific interest only.

Sulphuric acid, Acidum sulphuricum, $H_2SO_4 = 98$ (*Oil of vitriol, Hydrogen sulphate*). There is no other acid, and perhaps no other substance, manufactured by chemical action which is so largely used in chemical operations, and in the manufacture of so many of the most important articles, as is sulphuric acid.

Sulphuric acid was accidentally discovered in the fifteenth century, and was then obtained by heating ferrous sulphate (green vitriol) in a retort. To the liquid distilling over, the name of oil of vitriol was given, in allusion to the thick or oily appearance, and the green vitriol from which it was obtained.

Sulphuric acid is found in nature in combination with metals as sulphates. Thus calcium sulphate (gypsum), barium sulphate (heavy-spar), magnesium sulphate (Epsom salt), and others occur in nature.

Manufacture of sulphuric acid. Sulphuric acid is manufactured on a very large scale by passing into large leaden chambers simultaneously, the vapors of sulphur dioxide (obtained by burning sulphur or pyrites in furnaces), nitric acid, and steam, a supply of atmospheric air also being provided for. The most simple explanation that can be given for the manufacture of sulphuric acid is the fact that sulphur dioxide when treated with an oxidizing agent, in the presence of water, is converted into sulphuric acid:

$$SO_2 + O + H_2O = H_2SO_4.$$

Only a portion of the oxygen necessary for oxidation is derived from the nitric acid directly; the larger quantity is obtained from the atmospheric air, the oxides of nitrogen serving as agents for the transfer of the atmospheric oxygen.

By the action of nitric acid on sulphur dioxide and steam are formed sulphuric acid and nitrogen trioxide:

$$2SO_2 + H_2O + 2HNO_3 = 2H_2SO_4 + N_2O_3.$$

Nitrogen trioxide next takes up sulphur dioxide, water, and oxygen, forming a compound called nitrosyl-sulphuric acid:

$$2SO_2 + N_2O_3 + 2O + H_2O = 2(SO_2.OH.NO_2).$$

This complex compound is readily decomposed by steam into sulphuric acid and nitrogen trioxide:

$$2(SO_2.OH.NO_2) + H_2O = 2H_2SO_4 + N_2O_3$$

The nitrogen trioxide again forms nitrosyl-sulphuric acid, which again suffers decomposition, and so on indefinitely, as long as the constituents necessary for the changes are supplied. These facts show that a given quantity of nitric acid will convert an unlimited amount of sulphurous acid into sulphuric acid. There is, however, an unavoidable loss of small portions of nitric acid, or oxides of nitrogen, for which reason some nitric acid has to be supplied daily. It is likely that other chemical changes than the ones mentioned take place in the acid chamber, but according to modern investigations these are the principal ones.

The liquid sulphuric acid formed in the lead-chamber collects at the bottom of the chamber, whence it is drawn off. In this state it is known as chamber acid (specific gravity 1.50), and is not pure, but contains about 36 per cent. of water, and frequently either sulphurous or nitric acid. By evaporation in shallow leaden pans it is further concentrated, until it shows a specific gravity of 1.72. When this point is reached the acid acts upon the lead, wherefore the further concentration is conducted in vessels of glass or platinum, until a specific gravity of 1.84 is obtained. This acid contains about 95 per cent. of sulphuric acid; the remaining 5 per cent. of water cannot be expelled by heat.

Properties of sulphuric acid. Pure acid has a specific gravity of 1.848; it is a colorless liquid, of oily consistence, boiling at 338° C. (640° F.). It has a great tendency to combine with water, absorbing it readily from atmospheric air. Upon mixing sulphuric acid and water, heat is generated in consequence of the combination taking place between the two substances. To the same tendency of sulphuric acid to combine with water must be ascribed its property of destroying and blackening organic matter. Organic substances generally contain the elements carbon, hydrogen, and oxygen. Sulphuric acid added to such organic substances removes the elements hydrogen and oxygen (or at least a portion of them), combines them into water, with which it unites, leaving behind compounds so rich in carbon that the black color predominates. It is due to this decomposing action of sulphuric acid upon organic matter that traces of the latter color sulphuric acid dark yellow, brown, and, when present in larger quantities, almost black. The poisonous caustic properties are due to the same action.

Sulphuric acid is a very strong dibasic acid, which expels or displaces most other acids; its salts are known as sulphates.

The *sulphuric acid* of the U. S. P. should contain not less than 92.5 per cent. of H_2SO_4, corresponding to a specific gravity of not less than 1.835.

The *diluted sulphuric acid, Acidum sulphuricum dilutum,* is a mixture of 100 parts by weight of acid and 825 parts of water, or of about 60 c.c. of acid and 900 c.c. of water.

Tests for sulphuric acid and sulphates.

(Sodium sulphate, Na_2SO_4, may be used.)

1. Barium chloride produces a white precipitate of barium sulphate, insoluble in all acids:

$$Na_2SO_4 + BaCl_2 = BaSO_4 + 2NaCl.$$

2. Soluble lead salts (lead acetate) produce a white precipitate of lead sulphate, slightly soluble in hot concentrated acids and in ammonium acetate.

3. Sulphates, sulphur, or any compound containing it, fused on charcoal with sodium carbonate and potassium cyanide by means of a blowpipe, form *hepar* (chiefly sulphide of an alkali metal), which, when placed upon a silver coin and moistened with dilute hydrochloric acid, causes a black stain, due to the formation of silver sulphide. This test is of value in the case of insoluble sulphates, such as barium sulphate and others.

Antidotes. Magnesia, sodium carbonate, chalk, and soap, to neutralize the acid.

Sulpho-acids. Whilst but two oxides of sulphur exist in the separate state, there are a large number of sulpho-acids known. They are:

Hydrosulphuric acid,	H_2S.
Hyposulphurous acid,	H_2SO_2.
Sulphurous acid,	H_2SO_3.
Sulphuric acid,	H_2SO_4.
Pyrosulphuric acid,	$H_2S_2O_7$.
Thiosulphuric acid,	$H_2S_2O_3$.
Dithionic acid,	$H_2S_2O_6$.
Trithionic acid,	$H_2S_3O_6$
Tetrathionic acid,	$H_2S_4O_6$.
Pentathionic acid,	$H_2S_5O_6$.

Pyrosulphuric acid, $H_2S_2O_7$ (*Disulphuric acid, fuming sulphuric acid, Nordhausen oil of vitrol*). This acid is made by passing sulphur trioxide (obtained by heating ferrous sulphate) into sulphuric acid, when direct combination takes place:

$$H_2SO_4 + SO_3 = H_2S_2O_7.$$

It is a thick, highly corrosive liquid, which gives off dense fumes when exposed to the air, and decomposes readily into sulphur trioxide and sulphuric acid when heated.

Thiosulphuric acid, *formerly* **Hyposulphurous acid, $H_2S_2O_3$,** is of interest, because some of its salts are used, as, for instance, sodium thiosulphate, $Na_2S_2O_3$, the sodium hyposulphite of the U. S. P. The acid itself is not known in the separate state, since it decomposes into sulphur and sulphurous acid when attempts are made to liberate it from its salts.

Tests for thiosulphates.

(A solution of sodium thiosulphate, $Na_2S_2O_3$, may be used)

1. Thiosulphates liberate with sulphuric or hydrochloric acid sulphur dioxide, while sulphur is set free:

$$Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + H_2O + SO_2 + S.$$

2. Silver nitrate and barium chloride produce white precipitates of silver thiosulphate and barium thiosulphate. The silver salt becomes dark on heating; the barium salt is soluble in much water and is decomposed by hydrochloric acid.

Hydrogen sulphide, $H_2S = 34$. (*Hydrosulphuric acid, Sulphuretted hydrogen.*) This compound has been mentioned as being liberated by the decomposition of organic matter (putrefaction) and as a constituent of some spring waters. It is formed also during the destructive distillation of organic matter containing sulphur. The best mode of obtaining it is the decomposition of metallic sulphides by diluted sulphuric or hydrochloric acid. Ferrous sulphide is usually selected for decomposition:

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

Experiment 11. Use apparatus shown in Fig. 11, page 102. Place about 20 grammes of ferrous sulphide in the flask, cover the pieces with water, and add sulphuric or hydrochloric acid. Pass a portion of the washed gas into water, another portion into ammonia water. Use the solutions for the tests mentioned below. Ignite the gas at the delivery tube and notice that sulphur is deposited upon the surface of a cold plate held in the flame. Place the apparatus in the fume chamber during the operation. How much ferrous sulphide is required to liberate a quantity of hydrosulphuric acid sufficient to convert 1000 grammes of 10 per cent. ammonia water into ammonium sulphide solution? The reaction taking place is this:

$$2NH_3 + H_2S = (NH_4)_2S.$$

Hydrogen sulphide is a colorless gas, having an exceedingly offensive odor and a disgusting taste. Water absorbs about three volumes of the gas, and this solution is feebly acid. It is highly combustible in air, burning with a blue flame, and forming sulphur dioxide and water. It is directly poisonous when inhaled, its action depending chiefly on its power of reducing, and combining with, the blood-coloring matter. Plenty of fresh air, or air containing a very little chlorine, should be used as an antidote.

Hydrogen sulphide gas and its solution in water are frequently used as reagents in analytical chemistry for precipitating and recognizing metals. This use depends on the property of the sulphur to combine with many metals to form insoluble compounds, the color of which frequently is very characteristic:

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

The salts of hydrosulphuric acid are known as sulphides.

Tests for hydrogen sulphide or sulphides.

1. Hydrogen sulphide or soluble sulphides (ammonium sulphide may be used), when added to soluble salts of lead, copper, mercury, etc., give black precipitates of the sulphides of those metals.

2. From insoluble sulphides (ferrous sulphide, FeS, may be used) liberate the gas by sulphuric or hydrochloric acid, and test as above, or suspend a piece of filter-paper, moistened with solution of lead acetate, in the liberated gas, when the paper turns dark. Some sulphides, for instance those of mercury, gold, platinum, as also FeS_2, and a few others, are not decomposed by the acids mentioned, unless zinc be added.

Carbon disulphide, Carbonii bisulphidum, $CS_2 = 76$. This compound is obtained by passing vapors of sulphur over heated charcoal. It is a colorless, highly refractive, very volatile, and inflammable neutral liquid, having a characteristic odor and a sharp, aromatic taste. It boils at 46° C. (115° F.); it is almost insoluble in water, soluble in alcohol, ether, chloroform, fixed and volatile oils; for the latter two it is an excellent solvent, but dissolves, also, many other substances, such as sulphur, phosphorus, iodine, many alkaloids, etc.

Selenium, Se, and Tellurium, Te, are but rarely met with. Both elements show much resemblance to sulphur; both are polymorphous; both combine with hydrogen, forming H_2Se and H_2Te, gaseous compounds having an odor more disagreeable even than that of H_2S. Like sulphur, they form dioxides, SeO_2 and TeO_2, which combine with water, forming the acids H_2SeO_3 and H_2TeO_3, analogous to H_2SO_3. The acids H_2SeO_4 and H_2TeO_4, corresponding to H_2SO_4, also are known.

QUESTIONS.—131. How is sulphur found in nature? 132. Mention of sulphur: atomic weight, valence, color, odor, taste, solubility, behavior when heated, and allotropic modifications. 133. State the processes for obtaining sublimed, washed, and precipitated sulphur. 134. State composition and mode of preparing sulphur dioxide and sulphurous acid; what are they used for, and what are their properties? 135. Explain the process for the manufacture of sulphuric acid on a large scale. 136. Mention of sulphuric acid: color, specific gravity, its action on water and organic substances. 137. Give tests for sulphates and sulphites, sulphuric and sulphurous acids. 138. What is the difference between sulphates, sulphites, and sulphides? 139. How is hydrosulphuric acid formed in nature, and by what process is it obtained artificially? What are its properties, and what is it used for? 140. Mention antidotes in case of poisoning by sulphuric and hydrosulphuric acids.

15. PHOSPHORUS.

$P^{iii} = 31$ (30 96).

Occurrence in nature. Phosphorus is found in nature chiefly in the form of phosphates of calcium (*apatite, phosphorite*), iron, and aluminum, which minerals form deposits in some localities, but occur also diffused in small quantities through all soils upon which plants will grow, phosphorus being an essential constituent of the food of most plants. Through the plants it enters the animal system, where it is found either in organic compounds, or—and this in by far the greater quantity—as tricalcium phosphate principally in the bones, which contain about 60 per cent. of it. From the animal system it is eliminated chiefly in the urine.

Manufacture of phosphorus. Phosphorus was discovered and made first in 1669 by Brandt, of Hamburg, Germany, who obtained it in small quantities by distilling urine previously evaporated and mixed with sand.

The manufacture of phosphorus to-day depends on the deoxidation of metaphosphoric acid by carbon at a high temperature in retorts.

The acid is obtained by adding to any suitable tricalcium phophate sulphuric acid in a quantity sufficient to combine with the total amount of calcium present. The first action of sulphuric acid upon the phosphate consists in a removal of only two-thirds of the calcium present, and the formation of an acid phosphate:

$$Ca_3(PO_4)_2 + 3H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4 + H_2SO_4.$$

The nearly insoluble calcium sulphate is separated by filtration, and the solution of acid phosphate containing free sulphuric acid is evaporated to the consistency of a syrup, when more calcium sulphate separates and a solution of nearly pure phosphoric acid is left:

$$CaH_4(PO_4)_2 + H_2SO_4 = CaSO_4 + 2(H_3PO_4).$$

This syrupy phosphoric acid is mixed with coal and heated to a temperature sufficiently high to expel water and convert the ortho- into meta-phosphoric acid:

$$2(H_3PO_4) = 2HPO_3 + 2H_2O.$$

The dry solid mixture of this acid and charcoal is now introduced into retorts and heated to a strong red heat, when the following decomposition takes place:

$$2(HPO_3) + 5C = H_2O + 5CO + 2P.$$

The three products formed escape in the form of gases from the retort, and by passing them through cold water phosphorus is converted into a solid. The reaction in the retorts is somewhat more complicated than above stated in the equation, as some gaseous hydrogen phosphide and a few other products are formed in small quantities.

Properties of phosphorus. When recently prepared, phosphorus is a colorless, translucent, solid substance, which has somewhat the appearance and consistency of bleached wax. In the course of time, and especially on exposure to light, it becomes by degrees less translucent, opaque, white, yellow, and finally yellowish-red. At the freezing-point phosphorus is brittle; as the temperature increases it gradually becomes softer, until it fuses at 44° C. (111°F.), forming a yellowish fluid, which at 290° C. (554° F.) (in the absence of oxygen) is converted into a colorless vapor. Specific gravity 1.83 at 10° C. (50° F.)

The most characteristic features of phosphorus are its great affinity for oxygen, and its luminosity, visible in the dark, from which latter property its name, signifying "bearer of light," has been derived. In consequence of its affinity for oxygen, phosphorus has to be kept under water, as it invariably takes fire when exposed to the air, the slow oxidation taking place upon the surface of the phosphorus soon raising it to 50° C. (122° F.) at which temperature it ignites, burning with a bright white flame, and giving off dense, white fumes of phosphoric oxide. The luminosity of phosphorus, due to this slow oxidation, is seen when a piece of it is exposed to the air, and whitish vapors are emitted which are luminous in the dark; at the same time an odor resembling that of garlic is noticed.

Phosphorus is insoluble in water, sparingly soluble in alcohol, ether, fatty and essential oils, very soluble in chloroform and in disulphide of carbon, from which solution it separates in the form of crystals.

Phosphorus not only combines directly with oxygen, but also with chlorine, bromine, iodine, sulphur, and with many metals, the latter compounds being known as *phosphides*.

Phosphorus is trivalent in some compounds, as in PCl_3, P_2O_3; quinquivalent in others, as in PCl_5, P_2O_5.

The molecules of most elements contain two atoms; phosphorus is an exception to this rule, its molecule containing four atoms. The molecular weight of phosphorus is consequently $4 \times 31 = 124$.

Allotropic modifications. Several allotropic modifications of phosphorus are known, of which the *red phosphorus* (frequently called *amorphous phosphorus*) is the most important. This variety is obtained by exposing common phosphorus for about two days to a temperature of 260° C. (500° F.), in an atmosphere of carbon dioxide. Phosphorus is thereby gradually converted into a red powder, which differs widely from common phosphorus. It is not poisonous, not luminous, not soluble in the solvents above mentioned, not combustible until it has been heated to about 280° C. (536° F.), when it is reconverted into common phosphorus, which latter inflames at 50° C. (122° F.).

Use of phosphorus. By far the largest quantity of all phosphorus (both common and red) is used for matches, which are made by dipping wooden splints into some combustible substance, as melted sulphur or paraffin, and then into a paste made by thoroughly mixing phosphorus with glue in which some oxidizing agent (potassium nitrate or chlorate) has been dissolved.

Pharmaceutical preparations containing phosphorus in the elementary state are *phosphorated oil*, *pills of phosphorus*, and *spirit of phosphorus.*

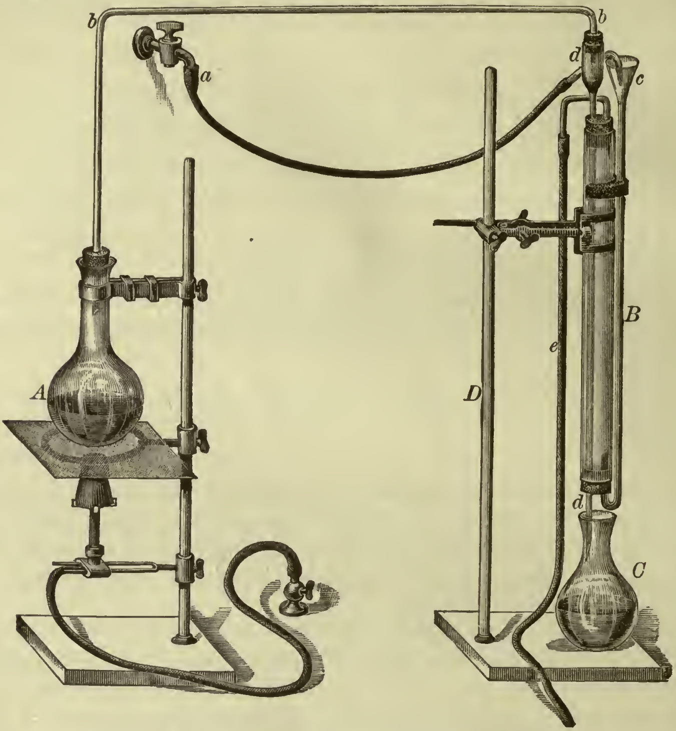
Phosphorus is used also for making phosphoric acid and other compounds.

Poisonous properties of phosphorus; antidotes. Common phosphorus is extremely poisonous, two kinds of phosphorus-poisoning being distinguished. They are the acute form, consequent upon the ingestion of a poisonous dose, and the chronic form affecting the workmen employed in the manufacture of phosphorus or of lucifer matches.

In cases of poisoning by phosphorus, efforts should be made to eliminate the poison as rapidly as possible by means of stomach-pump, emetics, or cathartics. As antidote a one-tenth per cent. solution of potassium permanganate has been used successfully; it acts by oxidizing the phosphorus, converting it into ortho-phosphoric acid. Oil of turpentine has also been used as an antidote, though its action has not been sufficiently explained. Oil or fatty matter (milk) must not be given, as they act as solvents of the phosphorus, causing its more ready assimilation.

Detection of phosphorus in cases of poisoning. Use is made of its luminous properties in detecting phosphorus, when in the elementary state. Organic matter (contents of stomach, food, etc.) containing phosphorus will often show this luminosity when agitated in the dark. If this process fails, in consequence of too small a quantity of the poison, a portion of the matter to be examined is rendered fluid by the addition of water, slightly acidulated with sulphuric acid, and placed in a flask, which is connected with a bent glass tube leading to a Liebig's condenser. The apparatus (Fig. 12) is placed in the dark, and the flask is heated. If phosphorus be present, a luminous ring will be seen where the glass tube, leading from the flask, enters the condenser. The heat should be raised gradually to the boiling-point, the liquid kept boiling for some time, and the products of distillation collected in a glass vessel. Phosphorus volatilizes with the steam, and small globules of it may be found in the collected fluid. If, however, the quantity of phosphorus in the examined matter was very small, it may all have become oxidized during the distillation, and the fluid will then contain phosphorous acid, the tests for which will be stated below.

FIG. 12.



Apparatus for detection of phosphorus in cases of poisoning.

It should be mentioned that the luminosity of phosphorus vapors is diminished, or even prevented, by vapors of essential oils (oil of turpentine, for instance), ether, olefiant gas, and a few other substances.

Oxides of phosphorus. Two oxides of phosphorus are known in the separate state. They are *phosphorus trioxide* or *phosphorous oxide*, P_2O_3, and *phosphorus pentoxide* or *phosphoric oxide*, P_2O_5. The first is obtained by slow oxidation of phosphorus, the second by burning phosphorus in dry air or oxygen. Both oxides are white solids, which combine readily with water, forming the four acids mentioned below.

No oxides corresponding to hypophosphorous acid, H_3PO_2, and hypophosphoric acid, H_2PO_3, are known.

Phosphorous acid, $H_3PO_3 = 82$. This acid is obtained by dissolving phosphorous oxide in water :

$$P_2O_3 + 3H_2O = 2H_3PO_3.$$

It is a colorless, acid liquid, which forms salts known as phosphites; it is a strong deoxidizing agent, easily absorbing oxygen, forming phosphoric acid.

Tests for phosphorous acid.

1. Added to mercuric chloride, a white precipitate of mercurous chloride is formed.
2. Added to silver nitrate, a black precipitate of metallic silver is produced.
3. After being heated with nitric acid, it shows reactions of phosphoric acid.

Phosphoric acids. Phosphoric oxide is capable of combining chemically with one, two, or three molecules of water, forming thereby three different acids.

$P_2O_5 + H_2O = H_2P_2O_6 = 2HPO_3$ Metaphosphoric acid.
$P_2O_5 + 2H_2O = H_4P_2O_7$ Pyrophosphoric acid.
$P_2O_5 + 3H_2O = H_6P_2O_8 = 2H_3PO_4$ Orthophosphoric acid.

These three acids show different reactions, act differently upon the animal system, and form different salts.

Metaphosphoric acid, $HPO_3 = 80$ (*Glacial phosphoric acid*). This acid is always formed when phosphoric oxide is dissolved in water; gradually, and more rapidly on heating with water, it absorbs the latter, forming orthophosphoric acid; by evaporating the latter sufficiently, metaphosphoric acid is re-formed.

Metaphosphoric acid is a monobasic acid which coagulates albumin (pyro- and orthophosphoric acids do not) and gives a white precipitate with ammonio-silver nitrate; it is not precipitated by magnesium sulphate in the presence of ammonia and ammonium chloride. It acts as a poison, whilst common phosphoric acid is comparatively harmless.

Pyrophosphoric acid, $H_4P_2O_7 = 178$. This is a tetra-basic acid which gives a white precipitate with ammonio-silver nitrate, whilst orthophosphoric acid gives a yellowish precipitate; it is not precipitated by ammonium molybdate, and does not coagulate albumin.

Phosphoric acid, Orthophosphoric acid, Acidum phosphoricum $H_3PO_4=98$ (*Trihydric phosphate, Common or tribasic phosphoric acid*). Nearly all phosphates found in nature are orthophosphates.

Phosphoric acid may be made by burning phosphorus, dissolving the phosphoric oxide in water, and boiling for a sufficient length of time to convert the meta- into orthophosphoric acid.

Experiment 12. Place a piece of phosphorus (about 0.5 gramme), after having dried it quickly between filter paper, in a small porcelain dish, standing upon a glass plate; ignite the phosphorus by touching it with a heated wire, and place over the dish an inverted large beaker. The white vapors of phosphoric oxide soon condense into flakes, which fall on the glass plate. Collect the white mass with a glass rod, and dissolve in a few c.c. of water. Use a portion of the solution for tests of metaphosphoric acid; evaporate the remaining quantity in a porcelain dish until it becomes syrupy, dilute with water and use it for making tests for orthophosphoric acid, either as such or after having neutralized with sodium carbonate. How much phosphorus is needed to make 490 grammes of the U.S.P. 50 per cent. phosphoric acid?

Phosphoric acid is also made by gently heating pieces of phosphorus with diluted nitric acid, when the phosphorus is oxidized, red fumes of nitrogen tetroxide escaping:

$$3P + 5HNO_3 + 2H_2O = 3H_3PO_4 + 5NO.$$

The liquid is evaporated until the excess of nitric acid has been expelled, and enough of water added to obtain an acid which contains 85 per cent. of the pure H_3PO_4. Specific gravity 1.710.

Diluted phosphoric acid, U.S.P., is made by mixing 100 c.c. of the 85 per cent. acid with 750 c c. of water. It contains 10 per cent. of absolute orthophosphoric acid.

Phosphoric acid is a colorless, odorless, strongly acid liquid, which, on heating, loses water, and finally is volatilized at a low red heat. It is a tribasic acid, forming three series of salts, namely:

Na_3PO_4 = Trisodium phosphate.
Na_2HPO_4 = Disodium hydrogen phosphate.
NaH_2PO_4 = Sodium dihydrogen phosphate.

If the metal be bivalent, the formulas are thus:

$Ca_3(PO_4)_2$ = Tricalcium phosphate.
$Ca_2H_2(PO_4)_2$ = Dicalcium orthophosphate.
$CaH_4(PO_4)_2$ = Monocalcium orthophosphate.

According to the number of hydrogen atoms replaced in the acid, the salts formed are also termed *primary, secondary,* and *tertiary* phosphates; KH_2PO_4 being, for instance, primary potassium phosphate; Na_2HPO_4 secondary sodium phosphate; Ag_3PO_4 tertiary silver phosphate.

Tests for phosphoric acid and phosphates.

(Sodium phosphate, Na_2HPO_4, may be used.)

1. Add to phosphoric acid, or to an aqueous solution of a phosphate, a mixture of magnesium sulphate, ammonium chloride, and ammonia water; a white crystalline precipitate falls, which is dimagnesium ammonium phosphate:

$$H_3PO_4 + MgSO_4 + 3NH_4OH = MgNH_4PO_4 + (NH_4)_2SO_4 + 3H_2O;$$
$$Na_2HPO_4 + MgSO_4 + NH_4OH = MgNH_4PO_4 + Na_2SO_4 + H_2O.$$

2. Add to a neutral solution of a phosphate, silver nitrate; a yellow precipitate of silver phosphate is produced, which is soluble both in ammonia and nitric acid:

$$Na_3PO_4 + 3AgNO_3 = Ag_3PO_4 + 3NaNO_3.$$

3. Add to phosphoric acid, or to a phosphate dissolved in water or in nitric acid, an excess of a solution of ammonium molybdate in dilute nitric acid, and apply heat; a yellow precipitate of phosphomolybdate of ammonium, $(NH_4)_3PO_4.10MoO_3.2H_2O$, is produced; the precipitate is readily soluble in ammonia water. This test is by far the most delicate, and even traces of phosphoric acid may be recognized by it; moreover, it can be used in an acid solution, while the first two tests cannot.

4. Add to a neutral solution of a phosphate, calcium or barium chloride; a white precipitate of calcium or barium phosphate is produced, which is soluble in acids.

5. Ferric chloride produces in neutral solution a yellowish-white precipitate of ferric phosphate, $Fe_2(PO_4)_2$, thus:

$$2Na_2HPO_4 + Fe_2Cl_6 = Fe_2(PO_4)_2 + 4NaCl + 2HCl.$$

The liberated hydrochloric acid dissolves some of the precipitate, which may be avoided by adding previously some sodium acetate; the hydrochloric acid combines with the sodium of the acetate, and the acetic acid which is set free has no dissolving action upon the ferric phosphate.

Hypophosphorous acid, H_3PO_2, or HPH_2O_2. When phosphorus is heated with solution of potassium, sodium, or calcium hydroxide, the hypophosphite of these metals is formed, while gaseous hydrogen phosphide, PH_3, is liberated and ignites spontaneously. The action may be represented thus:

$$3KOH + 4P + 3H_2O = 3KPH_2O_2 + PH_3.$$

or

$$3Ca(OH)_2 + 8P + 6H_2O = 3Ca(PH_2O_2)_2 + 2PH_3.$$

From calcium hypophosphite the acid may be obtained by decomposing the salt with oxalic acid, which forms insoluble calcium oxalate, while hypophosphorous acid remains in solution:

$$Ca(PH_2O_2)_2 + H_2C_2O_3 = CaC_2O_3 + 2HPH_2O_2.$$

From potassium hypophosphite the acid may be liberated by the addition of tartaric acid and alcohol, when potassium acid tartrate forms, which is nearly insoluble in dilute alcohol and may be separated by filtration.

Pure hypophosphorous acid is a white crystalline substance, acting energetically as a deoxidizing agent. Although containing three atoms of hydrogen, it is a monobasic acid, only one of the hydrogen atoms being replaceable by metals.

The *diluted hypophosphorous acid, Acidum hypophosphorosum dilutum* of the U.S.P., contains 10 per cent. of absolute acid. It is a colorless acid liquid, which, upon heating, loses water and is afterward decomposed into phosphoric acid and hydrogen phosphide, which ignites:

$$2HPH_2O_2 = H_3PO_4 + PH_3.$$

Tests for hypophosphites.

(Sodium hypophosphite, $NaPH_2O_2$, may be used.)

1. Heated over a flame they burn with a phosphorescent light, in consequence of their decomposition into inflammable hydrogen phosphide and a phosphate.
2. From solutions of mercuric chloride and silver nitrate they precipitate the metals in consequence of the deoxidizing action of hypophosphorous acid.
3. With zinc and diluted sulphuric acid they evolve hydrogen and phosphoretted hydrogen.
4. An acid solution of potassium permanganate is readily decolorized.
5. Ammonium molybdate solution produces a blue precipitate; a green color would indicate the presence of a phosphate, which alone gives a yellow precipitate with the reagent.

Hydrogen phosphide, PH_3 (*Phosphoretted hydrogen, phosphine*). The formation of this compound has been mentioned in the previous paragraph. It is a colorless, badly smelling, poisonous gas, which when generated as directed above, is spontaneously inflammable. This last-named property is due to the presence of small quantities of another compound of phosphorus and hydrogen which has the composition P_2H_4, and is spontaneously inflammable, while the compound PH_3 is not.

Hydrogen phosphide corresponds to the analogous composition of ammonia, NH_3. While the latter is readily soluble in water, and has strong basic properties, hydrogen phosphide is but sparingly soluble in water, and its basic properties are very weak. However, a few salts, such as the phosphonium chloride, PH_4Cl, analogous to ammonium chloride, NH_4Cl, are known.

16. CHLORINE.

$Cl^i = 35.4$ (35.37).

Haloids or Halogens. The four elements, fluorine, chlorine, bromine, and iodine, which form a natural group of elements, are known as haloids or halogens. The relation shown by the atomic weights of these four elements has been mentioned in connection with the consideration of natural groups of elements generally (see page 63). In many other respects a resemblance or relation can be discovered. For instance: All haloids are univalent elements, they combine with hydrogen, forming the acids HF, HCl, HBr, HI; they combine directly with most metals, forming fluorides, chlorides, bromides, and iodides. The relative combining energy lessens as the atomic weight increases; fluorine with the lowest atomic weight having the greatest, iodine with the highest atomic weight the smallest, affinity for other elements. The first two members of the group are gases, the third (bromine) is a liquid, the last (iodine) a solid, at ordinary temperature. They all show a distinct color in the gaseous state, have a disagreeable odor, and possess disinfecting properties.

Occurrence in nature. Chlorine is found chiefly as sodium chloride or common salt, NaCl, either dissolved in water (small quantities in almost every spring water, larger quantities in some mineral waters, and the principal amount in sea-water), or as solid deposits in the interior of the earth as *rock salt.*

QUESTIONS.—141. In what forms of combination is phosphorus found in nature? 142. Give an outline of the process for manufacturing phosphorus. 143. What are the symbol, valence, atomic and molecular weights of phosphorus? 144. State the chemical and physical properties both of common and red phosphorus. 145. By what methods may phosphorus be detected in cases of poisoning? 146. What two oxides of phosphorus are known; what is their composition, and what four acids do they form by combining with water? 147. State the official process for making phosphoric acid, and what are its properties? 148. By what tests may the three phosphoric acids be recognized and distinguished from phosphorous acid? 149. What is a phosphide, phosphite, phosphate, and hypophosphite? 150. What is glacial phosphoric acid, and in what respect does its action upon the animal system differ from the action of common phosphoric acid.

Other chlorides, such as those of potassium, magnesium, calcium, also are found in nature. As common salt, chlorine enters the animal system, taking there an active part in many of the physiological and chemical changes.

Preparation of chlorine. Most methods of liberating chlorine depend on an oxidation of the hydrogen of hydrochloric acid by suitable oxidizing agents, the hydrogen being converted into water, whilst chlorine is set free.

As oxidizing agents, may be used potassium chlorate, potassium bichromate, potassium permanganate, chromic acid, nitric acid, and many other substances.

The most common and cheapest mode of obtaining chlorine is to heat manganese dioxide, usually called black oxide of manganese, with hydrochloric acid, or a mixture of manganese dioxide and sodium chloride with sulphuric acid :

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + 2Cl.$$

Chlorine is liberated also by the action of sulphuric or hydrochloric acid on bleaching-powder, which is a mixture of calcium chloride and calcium hypochlorite :

$$CaCl_2.Ca(ClO)_2 + 2H_2SO_4 = 2CaSO_4 + 2H_2O + 4Cl.$$

Experiment 13. Use apparatus as in Fig. 8, page 86. Conduct operation in a fume-chamber. Place about 50 grammes of manganese dioxide in coarse powder in the flask, cover it with hydrochloric acid, shake up well to insure that no dry powder be left at the bottom of the flask, apply heat, and collect the gas in dry bottles by downward displacement. Keep the bottles loosely covered with pieces of stiff paper while filling them. Use the gas for the following experiments :

a. Fill a test-tube with chlorine, a second test-tube of same size with hydrogen; place them over one another so that the gases mix by diffusion, then hold them near a flame; a rapid combustion or explosion ensues.

b. Hold in one of the bottles filled with chlorine a lighted wax candle, and notice that it continues to burn with liberation of carbon. The hydrogen contained in the wax is in this case the only constituent of the wax which burns, *i. e.*, combines with chlorine.

c. Moisten a paper with oil of turpentine, $C_{10}H_{16}$, and drop it into another bottle filled with the gas; combustion ensues spontaneously, a black smoke of carbon being liberated.

d. Drop some finely powdered antimony into another bottle, and notice that each particle of the metal burns while passing through the gas, forming white antimonous chloride, $SbCl_3$.

e. Pass some chlorine gas into water, and suspend in the chlorine water thus formed colored flowers or pieces of dyed cotton, and notice that the color fades and in many cases disappears completely in a few hours.

Properties. Chlorine is a yellowish-green gas, having a disagreeable taste and an extremely penetrating, suffocating odor, acting energetically upon the air-passages, producing violent coughing and inflammation. It is about two and a half times heavier than air, soluble in water, and convertible into a greenish-yellow liquid by a pressure of about six atmospheres.

Chemically, the properties of chlorine are well marked, and there are but few elements which have as strong an affinity for other elements as chlorine; it unites with all of them directly, except with oxygen, nitrogen, and carbon, but even with these it may be made to combine indirectly. The act of combination between chlorine and other elements is frequently attended by the evolution of so much heat that light is produced, or, in other words, combustion takes place. Thus, hydrogen, phosphorus, and many metals burn easily in chlorine. The affinity between chlorine and hydrogen is intense, a mixture of the two gases being highly explosive. Such a mixture, kept in the dark, will not undergo chemical change, but when ignited, or when exposed to direct sunlight, the combination occurs instantly with an explosion. The affinity of chlorine for hydrogen is also demonstrated by its property of decomposing water, ammonia, and many hydrocarbons (compounds of carbon with hydrogen), such as oil of turpentine, $C_{10}H_{16}$, and others:

$$\begin{aligned} H_2O &+ 2Cl = 2HCl + O. \\ NH_3 &+ 3Cl = 3HCl + N. \\ C_{10}H_{16} &+ 16Cl = 16HCl + 10C. \end{aligned}$$

As shown by these formulas, hydrochloric acid is formed, whilst the other elements are set free.

Chlorine is a strong disinfecting, deodorizing, and bleaching agent; it acts as such either directly by combining with certain elements of the coloring or odoriferous matter, or, indirectly, by decomposing water with liberation of oxygen, which in the nascent state—that is, at the moment of liberation—has a strong tendency to oxidize other substances.

Chlorine water, Aqua chlori, is water saturated with pure chlorine at a temperature of about 10° C. (50° F.). One volume of water absorbs at that temperature about two volumes of chlorine, which is equal to 0 4 per cent. by weight. Chlorine water is a greenish-yellow liquid, having the odor and taste of chlorine. It must be kept in the dark, as otherwise decomposition takes place.

Hydrochloric acid, Acidum hydrochloricum, $HCl = 36.4$ (*Chlorhydric acid, Muriatic acid, Hydrogen chloride*). One volume of hydrogen combines with one volume of chlorine to form two volumes of hydrochloric acid:

Another method for obtaining it is the decomposition of a chloride by sulphuric acid:

$$NaCl + H_2SO_4 = HCl + NaHSO_4;$$

or

$$2NaCl + H_2SO_4 = 2HCl + Na_2SO_4.$$

Experiment 14. Use apparatus as in Fig. 8, page 86. Place about 20 grammes of sodium chloride into the flask (which should be provided with a funnel-tube) and add about 30 c.c. of concentrated sulphuric acid; mix well, apply heat, and pass the gas into water for absorption. If a pure acid be desired, the gas has to be passed through water contained in a wash-bottle; apparatus shown in Fig. 11, page 102, may then be used. Use the acid made for tests mentioned below. How much of the U. S. P. 31.9 per cent. hydrochloric acid can be made from 117 pounds of sodium chloride?

Hydrochloric acid is a colorless gas, has a sharp, penetrating odor, and is very irritating when inhaled. It is neither combustible nor a supporter of combustion, and has great affinity for water, which property is the cause of the formation of white clouds whenever the gas comes in contact with the vapors of water, or with moist air; the white clouds being formed of minute particles of liquid hydrochloric acid.

Whilst hydrochloric acid is a gas, this name is used also for its solution in water, one volume of which at ordinary temperature takes up over 400 volumes of the gas.

The hydrochloric acid of the U. S. P. is an acid containing 31.9 per cent. of HCl. It is a colorless, fuming liquid, having the odor of the gas, strong acid properties, and a specific gravity of 1.163. The official diluted hydrochloric acid is made by mixing 100 parts by weight of the above acid with 219 parts of water. It contains 10 per cent. of HCl.

The same antidotes may be used as for nitric acid.

Tests for hydrochloric acid and chlorides.

(Sodium chloride, NaCl, may be used.)

1. To hydrochloric acid, or to solution of chlorides, add silver nitrate: a white, curdy precipitate is produced, which is soluble in ammonia water, but insoluble in nitric acid:

$$AgNO_3 + NaCl = NaNO_3 + AgCl;$$
$$AgNO_3 + HCl = HNO_3 + AgCl.$$

2. Add solution of mercurous salt (mercurous nitrate): a white precipitate is produced, which blackens on the addition of ammonia:

$$Hg_2 2NO_3 + 2NaCl = 2NaNO_3 + Hg_2Cl_2.$$

3. Add solution of lead acetate: a white precipitate of lead chloride is formed, which is soluble in hot, or in much cold water, and is, therefore, not formed in dilute solutions.

4. To a dry chloride add strong sulphuric acid and heat: hydrochloric acid gas is evolved, which may be recognized by the odor, or by its action on silver nitrate.

5. Chlorides treated with sulphuric acid and manganese dioxide evolve chlorine.

Nitro-hydrochloric acid, Aqua regia (*Nitro-muriatic acid*). Obtained by mixing 40 c.c. of nitric acid with 180 c.c. of hydrochloric acid. The two acids act chemically upon each other, forming chloronitrous or chloronitric gas, chlorine, and water:

$$HNO_3 + 3HCl = NOCl + 2H_2O + 2Cl,$$
$$HNO_3 + 3HCl = NOCl_2 + 2H_2O + Cl.$$

The dissolving power of this acid upon gold and platinum depends on the action of the free chlorine and the action of the chloronitrous and chloronitric gases, both of which part easily with their chlorine.

The official *diluted nitro-hydrochloric acid* is made by mixing the acids in the quantities above mentioned and adding, when effervescence has ceased, 780 c.c. of water.

Compounds of chlorine with oxygen. There is no method known by which to combine chlorine and oxygen directly, all the compounds formed by the union of these elements being obtained by indirect processes. The oxides of chlorine are the following:

Chlorine monoxide or hypochlorous oxide,	Cl_2O.
Chlorine trioxide or chlorous oxide,	Cl_2O_3.
Chlorine dioxide,	ClO_2.

All these oxides are yellow or greenish-yellow gases; the first and second combine with water, forming the hypochlorous and chlorous acids:

$$Cl_2O + H_2O = 2HClO.$$
$$Cl_2O_3 + H_2O = 2HClO_2.$$

The oxides Cl_2O_5 and Cl_2O_7 from which chloric acid, $HClO_3$, and perchloric acid, $HClO_4$, might be formed, are not known. The chlorine oxides, the acids, and many of their salts are distinguished by the great facility with which they decompose, frequently with violent explosion, for which reason care must be taken in the preparation and handling of these compounds.

Chlorine acids.

Hydrochloric acid,	HCl.
Hypochlorous acid,	$HClO$.
Chlorous acid,	$HClO_2$.
Chloric acid,	$HClO_3$.
Perchloric acid,	$HClO_4$.

With the exception of hydrochloric acid, which has been considered, none of the five acids is of practical interest as such, but many of the salts of hypochlorous and chloric acids, known as hypochlorites and chlorates respectively, are of great and general importance.

Hypochlorous acid, $HClO$, may be obtained by the action of chlorine water on mercuric oxide, insoluble mercuric oxychloride being formed also:

$$2HgO + 4Cl + H_2O = Hg_2OCl + 2HClO.$$

Hypochlorous acid is a colorless, monobasic acid possessing strong bleaching properties.

Hypochlorites are formed by the action of chlorine on the hydroxides of potassium, sodium, calcium, etc., at the ordinary temperature:

$$2NaOH + 2Cl = NaCl + NaClO + H_2O.$$

Chloric acid, $HClO_3$, may be obtained from potassium chlorate by the action of hydrofluosilicic acid; it is, however, an unstable substance which will decompose, frequently with a violent explosion. Chlorates are generally obtained by the action of chlorine on alkali hydroxides at a temperature of about 100° C. (212° F.)

$$6KOH + 6Cl = 5KCl + KClO_3 + 3H_2O.$$

Mixtures of hypochlorites and chlorides are converted into chlorates by boiling their solution:

$$3KCl + 3KClO = 5KCl + KClO_3.$$

Tests for chlorates and hypochlorites.

(Potass. chlorate, $KClO_3$, and bleaching powder, $Ca2ClO.CaCl_2$, may be used.)

1. Chlorates liberate oxygen when heated by themselves.

2. Chlorates liberate chlorous tetroxide, Cl_2O_4, a deep-yellow explosive gas, on the addition of strong sulphuric acid.

3. Chlorates deflagrate when sprinkled on red-hot charcoal.

4. Hypochlorites evolve a peculiarly smelling gas (hypochlorous acid) on the addition of acids, and are strong bleaching agents.

17. BROMINE—IODINE—FLUORINE.

Bromine, Bromum, Br = 79.8. This element is found in sea-water and many mineral waters, chiefly as magnesium bromide, which compound, however, represents in all these waters a comparatively small percentage of the total quantity of the different salts present. Most of these salts are separated from the water by evaporation and crystallization, and the remaining mother-liquor, containing the magnesium bromide, is treated with chlorine, which liberates bromine, the vapors of which are condensed in cooled receivers:

$$MgBr_2 + 2Cl = MgCl_2 + 2Br.$$

Bromine is at common temperature a heavy, dark reddish-brown liquid, giving off yellowish-red fumes of an exceedingly suffocating and irritating odor; it is very volatile, freezes at about —24° C. (—11° F.), and has a specific gravity of 2.99; it is soluble in 30 parts of water, more freely in alcohol, abundantly in ether and bisulphide of carbon; it is a strong disinfectant, and its aqueous solution is also a bleaching agent.

Hydrobromic acid, Acidum hydrobromicum, HBr = 80.8. This acid cannot well be obtained by the action of concentrated sulphuric acid upon bromides, since the hydrobromic acid first formed

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Questions.—151. State the names and general physical and chemical properties of the four halogens. 152. How is chlorine found in nature, and why does it not occur in a free state? 153. State the general principle for liberating chlorine from hydrochloric acid, and explain the action of the latter on manganese dioxide. 154. Mention of chlorine: its atomic weight, molecular weight, valence, color, odor, action when inhaled, and solubility in water. 155. How does chlorine act chemically upon metals, hydrogen, phosphorus, water, ammonia, hydrocarbons, and coloring matters? 156. Mention two processes for making hydrochloric acid; state its composition, properties, and tests by which it may be recognized. 157. What is aqua regia? 158. State the composition of hypochlorous and chloric acids. 159. What is the difference in the action of chlorine upon a solution of potassium hydroxide at ordinary temperature and at the boiling-point? 160. How many pounds of manganese dioxide, and how many of hydrochloric acid gas are required to liberate 142 pounds of chlorine?

becomes readily decomposed with formation of sulphur dioxide and free bromine. Thus:

$$2NaBr + H_2SO_4 = 2HBr + Na_2SO_4;$$
$$2HBr + H_2SO_4 = 2Br + SO_2 + 2H_2O.$$

If, however, dilute sulphuric acid is added to a warm solution of potassium bromide, potassium sulphate is formed, a portion of which crystallizes on cooling. From the remaining portion of the salt, the hydrobromic acid may be separated by distillation.

Hydrobromic acid may also be obtained by the formation of bromide of phosphorus, PBr_5 (the two elements combine directly), and its decomposition by water:

$$PBr_5 + 4H_2O = 5HBr + H_3PO_4.$$

In the form of solution this acid may be prepared also by treating bromine under water with hydrosulphuric acid until the brown color of bromine has entirely disappeared. The reaction is as follows:

$$10Br + 2H_2S + 4H_2O = 10HBr + H_2SO_4 + S.$$

The liquid is filtered from the sulphur and separated from the sulphuric acid by distillation.

Hydrobromic acid is, like hydrochloric acid, a colorless gas, of strong acid properties, easily soluble in water.

Diluted hydrobromic acid, Acidum hydrobromicum dilutum, is a solution of 10 per cent. of hydrobromic acid in water. It is a colorless, odorless, acid liquid of the specific gravity 1.077.

Hypobromic acid, HBrO; Bromic acid, $HBrO_3$, and their salts, the *hypobromites* and *bromates*, are analogous to the corresponding chlorine compounds, and may be obtained by analogous processes.

Tests for Bromides.

(Potassium bromide, KBr, may be used.)

1. Silver nitrate produces in solutions of bromides a slightly yellowish-white precipitate of silver bromide, insoluble in nitric acid, sparingly soluble in ammonium hydroxide.
2. Addition of chlorine water, or heating with nitric acid, liberates bromine, which may be dissolved by shaking with chloroform or ether.
3. Mucilage of starch added to the liberated bromine is colored yellow.
4. A crystal of potassium bromide dropped into an acidified solution of cupric sulphate produces a deep red-brown coloration of cupric bromide, $CuBr_2$.
5. Strong sulphuric acid added to a dry bromide liberates hydro-

bromic acid, HBr, a portion of which decomposes with liberation of yellowish-red vapors of bromine. See explanation above.

Iodine, Iodum, I = 126.53. Iodine is found in nature in combination with sodium and potassium, in some spring waters and in sea-water, from which latter it is taken up by sea-plants and many aquatic animals. Iodine is derived chiefly from the ashes of seaweeds known as *kelp*. By washing these ashes with water, the soluble constituents are dissolved, the larger quantities of sodium chloride, sodium and potassium carbonates are removed by evaporation and crystallization, and from the remaining mother-liquor iodine is obtained by treating the liquor with manganese dioxide and hydrochloric (or sulphuric) acid:

$$2KI + MnO_2 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 2H_2O + 2I.$$

The liberated iodine distils, and is collected in cooled receivers. Sodium nitrate found in Chili contains a small quantity of sodium iodate, and the mother-liquors, from which the nitrate has been crystallized, contain enough iodate to be employed for the preparation of iodine.

Iodine is a bluish-black, crystalline substance of a somewhat metallic lustre, a distinctive odor, a sharp and acrid taste, and a neutral reaction. Specific gravity 4.948 at 17° C. (62.6° F.). It fuses at 114° C. (237° F.), and boils at 180° C. (356° F.), being converted into beautiful purple-violet vapors; also, it volatilizes in small quantities at ordinary temperature. It is soluble in about 5000 parts of water, more soluble in water containing salts, for instance, potassium iodide; it is soluble in 10 parts of alcohol (*tincture of iodine*), very soluble in ether, bisulphide of carbon, and chloroform. The solution of iodine in alcohol or ether has a brown, the solution in disulphide of carbon or in chloroform a violet color. Iodine stains the skin brown, and when taken internally acts as an irritant poison.

Hydriodic acid, Hydrogen iodide, HI. This is a colorless gas readily soluble in water; the solution is unstable, being easily decomposed with liberation of iodine. It may be obtained by processes analogous to those mentioned for the preparation of hydrobromic acid. The action of hydrosulphuric acid upon iodine in the presence of water is as follows:

$$H_2S + 2I = 2HI + S.$$

Another method depends on the decomposition of an aqueous solution of potassium iodide by an alcoholic solution of tartaric acid.

Upon cooling the mixture to the freezing-point, acid potassium tartrate separates, while hydriodic acid remains in solution:

$$KI + H_2C_4H_4O_6 = KHC_4H_4O_6 + HI.$$

Whilst hydriodic acid itself is not of much importance, many of its salts, the iodides, are of great interest.

Tests for iodine and iodides.

(Potassium iodide, KI, may be used.)

1. Add to free iodine (or to an iodide, after it has been decomposed by a few drops of chlorine water, or by strong nitric acid) mucilage of starch: a dark-blue color is produced, due to the formation of "blue iodized starch."

2. From solution of an iodide liberate iodine by adding chlorine water, or nitric acid containing a little nitrous acid, and shake the solution with disulphide of carbon or chloroform. After standing a few minutes the liquids form a layer of a beautiful violet color.

3. Add to solution of an iodide, solution of silver nitrate: a pale yellow precipitate of silver iodide, AgI, falls, which is insoluble in nitric acid, and sparingly soluble in dilute ammonium hydroxide.

4. Add lead acetate to a neutral solution of an iodide: a yellow precipitate of lead iodide, PbI_2, is produced.

5. Add mercuric chloride to a neutral solution of an iodide: a red precipitate of mercuric iodide, HgI_2, is produced.

6. Add sulphuric acid: violet vapors of iodine are evolved.

Iodic acid, HIO_3. When iodine is dissolved in strong nitric acid, this solution being then evaporated to dryness and heated to about 200° C. (392° F.) a white residue remains, which is iodine pentoxide:

$$6I + 10HNO_3 = 5N_2O_2 + 5H_2O + 3I_2O_5.$$

By dissolving this oxide in water, iodic acid is obtained:

$$I_2O_5 + H_2O = 2HIO_3.$$

Iodic acid is a white crystalline substance, very soluble in water. From iodic acid or from iodates, sulphurous acid and many other reducing agents liberate iodine.

Sulphur iodide, Sulphuris iodidum, S_2I_2. When the two elements, sulphur and iodine, are mixed together in the proportion of their atomic weights, and this mixture is heated, direct combination takes place. The fused mass is grayish-black, brittle, has a crystalline fracture and a metallic lustre. It is almost insoluble in water, but soluble in glycerin and in carbon disulphide.

Fluorine, F = 19. This element is found in nature, chiefly as fluorspar, calcium flouride, CaF_2; traces of fluorine occur in many minerals, in some waters, and also in the enamel of teeth, and in the bones of mammals. Fluorine was, until 1887, scarcely known in the elementary state, because all attempts to isolate it were frustrated by the powerful affinities which this element possesses, and which render it difficult to obtain any material (from which a vessel may be made) which is not chemically acted upon, and, therefore, destroyed, by fluorine. The method used now for liberating fluorine depends upon the decomposition of hydrofluoric acid by a strong current of electricity in an apparatus constructed of platinum with stoppers of fluorspar. To prevent too rapid corrosion of the platinum vessels, the decomposition is accomplished at a temperature below the freezing-point. Fluorine is a gas of yellowish color, having a highly irritating and suffocating odor, and possessing affinities stronger than those of any other element. As a supporter of combustion, fluorine leaves oxygen far behind; it combines spontaneously even in the dark and at low temperature with hydrogen; sulphur, phosphorus, lampblack, and also many metals ignite readily in fluorine; even the noble metals, gold, platinum, and mercury, are converted into fluorides; from sodium chloride the chlorine is liberated with the formation of sodium fluoride; organic substances, such as oil of turpentine, alcohol, ether, and even cork ignite spontaneously when brought in contact with this remarkable element.

Hydrofluoric acid, HF (*Hydrogen fluoride*). A colorless gas, very irritating, soluble in water. It is obtained by the action of sulphuric acid on fluorspar:

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4.$$

Hydrofluoric acid, either in the gaseous state or its solution in water, is used for etching on glass. This effect is due to the action of the acid upon the silica of the glass, which is converted into either silicon fluoride, SiF_4; or into hydrofluosilicic acid, H_2SiF_6.

Hydrofluoric acid, or strong solutions of it, are powerful antiseptics. In small quantities the acid is used as an admixture to fermenting liquids, as it has been found that it does not act upon the principal ferment of yeast, which causes the decomposition of sugar into alcohol and carbon dioxide, while it readily destroys a number of objectionable ferments. The yield of alcohol is thus considerably increased.

Experiment 15. Prepare a glass plate by heating it slightly and covering its surface with a thin layer of wax or paraffin; after cooling, scratch some letters or figures through the wax, thus exposing the glass. Set the plate over a dish (one made of lead or platinum answers best), in which a few grammes of powdered fluorspar have been mixed with about an equal weight of sulphuric acid, and set in the open air for a few hours (heating slightly facilitates the action); upon removing the wax or paraffin, the glass will be found to be *etched* where its surface was exposed to the vapors of the acid. This experiment serves also as the best *test for fluorides.*

QUESTIONS.—161. How is bromine found in nature? 162. State the physical and chemical properties of bromine. 163. What is hydrobromic acid, and how can it be made? 164. By what tests may bromine and bromides be recognized? 165. What is the chief source of iodine? 166. What are the chemical and physical properties of iodine? 167. What is tincture of iodine, what is its color, and how does it stain the skin? 168. Mention reactions by which iodine and iodides may be recognized. 169. By what element may bromine and iodine be liberated from their compounds? 170. How is hydrofluoric acid made, and what is it used for?

IV.

METALS AND THEIR COMBINATIONS.

18. GENERAL REMARKS REGARDING METALS.

Of the total number of fifty-five metallic elements only about one-half are of sufficient general interest and importance to deserve consideration in this book.

Derivation of names, symbols, and atomic weights.

Aluminum,	Al	= 27.04.	From *alum*, a salt containing it.
Antimony, (Stibium.)	Sb	= 119.6.	From the Greek *ἀντὶ* (anti), against, and *moine*, a French word for monk, from the fact that some monks were poisoned by compounds of antimony. Stibium, from the Greek, *στίβι* (stibi), the name for the native sulphide of antimony.
Arsenicum,	As	= 74.9.	From the Greek *ἀρσενικὸν* (arsenicon), the name for the native sulphide of arsenic.
Barium,	Ba	= 136.9.	From the Greek *βαρὺς* (barys), heavy, in allusion to the high specific gravity of barium sulphate, or heavy-spar.
Bismuth,	Bi	= 208.9.	From the German *wismuth*, an expression used long ago by the miners in allusion to the variegated tints of the metal when freshly broken.
Cadmium,	Cd	= 111.5.	From the Greek *καδμεία* (kadmeia) the old name for calamine (zinc carbonate), with which cadmium is frequently associated.
Calcium,	Ca	= 39.91.	From the Latin *calx*, lime, the oxide of calcium.
Chromium,	Cr	= 52.0.	From the Greek *χρῶμα* (chroma), color, in allusion to the beautiful colors of all its compounds.
Cobalt,	Co	= 58.6.	From the German *Kobold*, which means a demon inhabiting the mines.
Copper,	Cu	= 63.18	From the Latin *cuprum*, copper, and this from the Island of Cyprus, where copper was first obtained by the ancients.
Gold, (Aurum.)	Au	= 196.7.	Gold means bright yellow in several old languages. The Latin *aurum* signifies the color of fire.
Iron,	Fe	= 55.88.	Iron probably means metal; the derivation of the Latin *ferrum* is not definitely known.

Lead, (Plumbum.)	Pb	= 206.4.	Both words signify something heavy.
Lithium,	Li	= 7.01.	From the Greek λίθειος (litheios), stony.
Magnesium,	Mg	= 24.3.	From Magnesia, a town in Asia Minor, where magnesium carbonate was found as a mineral.
Manganese,	Mn	= 54.8.	Probably from magnesium, with the compounds of which it was long confounded.
Mercury, (Hydrargyrum)	Hg	= 199.8.	From Mercury, the messenger of the Greek gods. Hydrargyrum means liquid silver.
Molybdenum,	Mo	= 95.9.	From the Greek μόλυβδος (molybdos), lead.
Nickel,	Ni	= 58.6.	From the old German word *nickel*, which means worthless.
Platinum,	Pt	= 194.3.	Platina is the diminutive of the Spanish word *plata*, silver.
Potassium, (Kalium.)	K	= 39.03.	From pot-ash; potassium carbonate being the chief constituent of the lye of wood-ashes. Kali is the Arabic word for ashes.
Silver, (Argentum.)	Ag	= 107.66.	Both words signify white.
Sodium, (Natrium.)	Na	= 23.0.	From soda-ash, or sod-ash, the ashes of marine plants which are rich in sodium carbonate. Natron is an old name for natural deposits of sodium carbonate.
Strontium,	Sr	= 87.3.	From Strontian, a village in Scotland, where strontium carbonate is found.
Tin, (Stannum.)	Sn	= 118.8.	Both words most likely signify stone.
Zinc,	Zn	= 65.1.	Most likely from the German *zinn* or *tin*, the metals having been confounded with each other.

Melting-points of metals.

		C.	F.
Fusible below the boiling-point of water,	Mercury	—40°	— 40°
	Potassium	+62	+144
	Sodium	97	207
Fusible below red heat,	Lithium	180	356
	Tin	228	443
	Cadmium	230	446
	Bismuth	260	500
	Lead	325	617
	Zinc	412	773
	Magnesium	455	850
	Antimony	620	1150
	Aluminum	700	1292
Unknown,	Barium.		
	Calcium.		
	Strontium.		
	Arsenic.		

Infusible below a red heat.	Silver	1020	1868	
	Copper	1100	2012	
	Gold	1200	2192	
	Cast-iron	1800	3272	
	Pure iron, Nickel, Cobalt, Manganese,			Highest heat of forge.
	Molybdenum, Chromium,			Agglomerate, but do not melt in forge.
	Platinum,			Fusible in the oxyhydrogen blowpipe flame.

Specific gravities of metals at 15.5° C.

Lithium	0.593	Manganese	8.00
Potassium	0.865	Molybdenum	8.63
Sodium	0.972	Cadmium	8.70
Calcium	1.57	Nickel	8.70
Magnesium	1.75	Cobalt	8.95
Strontium	2.54	Copper	8.96
Aluminum	2.67	Bismuth	9.90
Barium	4.00	Silver	10.50
Arsenic	5.88	Lead	11.36
Antimony	6.72	Mercury	13.59
Zinc	6.90	Gold	19.36
Tin	7.29	Platinum	21.50
Iron	7.79		

Time of discovery of the metals.

Gold, Silver, Mercury, Copper, Zinc, Tin, Iron, Lead,	These metals were known to the ancients, because either they are found in a metallic state, or can be obtained by comparatively simple processes from the oxides.
Antimony, Bismuth,	Latter part of the fifteenth century.
Arsenic,	1694, by Schröder.
Cobalt,	1733, by Brandt.
Platinum,	1741, by Wood.
Nickel,	1751, by Cronstedt.
Manganese,	1774, by Galm
Molybdenum,	1782, by Hjelm.
Chromium,	1797, by Vauquelin.

Potassium, Sodium, Barium, Calcium, Strontium, Magnesium,	1807–1808	H. Davy discovered methods for the separation of these metals from their oxides.
Cadmium,	1817, by Stromeyer.	
Lithium,	1817, by Arfvedson.	
Aluminum,	1828, by Wöhler.	

Valence of metals.

Univalent.

Lithium,
Potassium,
Sodium,
Silver.

Bi- and sexivalent.

Chromium,
Cobalt,
Iron,
Manganese,
Nickel.

Bivalent.

Barium,
Calcium,
Strontium,
Magnesium,
Cadmium,
Zinc,
Copper,
Mercury.

Bi- and quadrivalent

Lead,
Platinum,
Tin.

Trivalent.

Aluminum,
Bismuth,
Gold.

Tri- and quinquivalent.

Antimony,
Arsenic.

Sexivalent.

Molybdenum.

Occurrence in nature.

a. In a free or combined state.

Gold, Platinum,	Almost exclusively in the metallic state.
Silver, Mercury,	As metals or sulphides.

Bismuth, generally metallic, also as oxide and sulphide.
Copper, rarely metallic; chiefly as sulphide, oxide, and carbonate.

b. In combination only.

Potassium, Sodium, Lithium,	Chiefly as chlorides or silicates.

Barium, as sulphate.	
Calcium,	As carbonates, sulphates, silicates.
Strontium,	
Magnesium,	
Aluminum, in silicates.	
Iron,	As oxides, carbonates, sulphides.
Zinc,	
Cadmium,	
Arsenic,	Chiefly as sulphides.
Antimony,	
Lead,	
Cobalt,	
Nickel,	
Molybdenum,	
Chromium,	Chiefly as oxides.
Manganese,	
Tin,	

Classification of metals.

Light metals.	*Heavy metals.*
Sp. gr. from 0.6 to 4.	Sp gr. from 6 to 21.5.
Sulphides soluble in water.	Sulphides insoluble in water.

Light metals.

Earth metals.	*Alkaline earth metals.*	*Alkali-metal.*
Al, and many rare metals.	Ba, Ca, Sr, (Mg).	K, Na, Li, (NH_4).
Oxides insoluble.	Oxides soluble;	Oxides, carbonates, and most salts soluble.
	Carbonates insoluble.	

Heavy metals.

<table>
<tr><th>Arsenic group.</th><th>Lead group.</th><th>Iron group.</th></tr>
<tr><td>As, Sb, Sn, Au, Pt, Mo.</td><td>Pb, Cu, Bi, Ag, Hg, Cd.</td><td rowspan="2">Fe, Co, Ni, Mn, Zn, Cr.
Sulphides soluble in dilute acids.</td></tr>
<tr><td colspan="2">Sulphides insoluble in dilute acids.</td></tr>
<tr><td>Sulphides soluble in ammonium sulphide.</td><td>Sulphides insoluble in ammonium sulphide.</td><td></td></tr>
</table>

Properties of metals. All metals have a peculiar lustre known as metallic lustre, and all are good conductors of heat and electricity. The color of most metals is white, grayish, or bluish-white, or dark-gray; a few metals show a distinct color, as, for instance, gold and calcium (yellow), and copper (red).

At ordinary temperatures metals are solids with the exception of mercury, all are fusible, and some are so volatile that they may be distilled. Most, probably all, metals may be obtained in a crystallized condition.

The combinations of metals among themselves are called *alloys*, or, when mercury is one of the constituents, *amalgams*. These combinations, which usually may be obtained by fusing the metals together, must be looked upon as molecular mixtures, not as definite chemical compounds. All alloys still exhibit the metallic nature in their general physical characters. It is different, however, when metals combine with non-metals; in this case the metallic characters are lost almost invariably.

All metals combine with chlorine, fluorine, and oxygen; most metals also with sulphur, bromine, and iodine, forming the respective chlorides, fluorides, oxides, sulphides, bromides, and iodides. Metals replace hydrogen in acids, forming salts.

Most metals may be obtained from their oxides by heating the latter with charcoal, the carbon combining with the oxygen of the oxide, whilst the metal is liberated:

$$MO + C = CO + M;$$

or

$$2MO + C = CO_2 + 2M.$$

Also hydrogen may be used in some cases as the deoxidizing agent:

$$MO + 2H = H_2O + M.$$

Some metals are found in nature chiefly as sulphides, which usually are converted into oxides (before the metal can be obtained) by roasting. The term *roasting*, when used in metallurgy, means heating strongly in an oxidizing atmosphere, when the sulphides are converted into sulphates or oxides, thus:

$$MS + 4O = MSO_4;$$

or

$$MS + 3O = MO + SO_2.$$

19. POTASSIUM (KALIUM).

$K^{i} = 39$ (39 03).

General remarks regarding alkali-metals. The metals potassium, sodium, lithium (rubidium and cæsium) form the group of the

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QUESTIONS.—171. How many metals are known, and about how many are of general interest? 172. Mention some metals having very low and some having very high fusing-points. 173. What range of specific gravities do we find among the metals? 174. Mention some univalent and some bivalent metals; also some which show a different valence under different conditions. 175. Mention some metals which are found in nature in an uncombined state; some which are found as oxides, sulphides, chlorides, and carbonates, respectively. 176. Into what two groups are the metals divided? 177. State the three groups of light metals? 178. What is a metal? 179. What is an alloy, and what an amalgam? 180. By what process can most metals be obtained from their oxides?

alkali-metals, which, in many respects, show a great resemblance to each other in chemical and physical properties. For reasons to be explained hereafter, the compound radical ammonium is usually classed among the alkali-metals.

The alkali-metals are all univalent; they decompose water at the ordinary temperature, with liberation of hydrogen; they combine spontaneously with oxygen and chlorine; their hydroxides, sulphates, nitrates, phosphates, carbonates, sulphides, chlorides, iodides, and nearly all other of their salts are soluble in water; all these compounds are white, solid substances, many of which are fusible at a red heat. Of all metals, those of the alkalies are the only ones forming hydroxides and carbonates which are not decomposed by heat.

The metals themselves are of a silver-white color, and extremely soft; on account of their tendency to combine with oxygen they must be kept in a liquid not containing that element (coal-oil) or in an atmosphere of hydrogen.

The metals may be obtained by heating their carbonates with carbon in iron retorts, the escaping vapors being passed under coal-oil for condensation of the metal:

$$K_2CO_3 + 2C = 3CO + 2K.$$

Occurrence in nature. Potassium is found in nature chiefly as a double silicate of potassium and aluminum (granite rocks, feldspar, and other minerals), or as chloride and nitrate. By the gradual disintegration of the different granite rocks containing potassium silicate, this has entered into the soil, whence it is taken up by plants as one of the necessary constituents of their food.

In the plant potassium enters largely into combination with organic compounds (tartaric acid, citric acid, etc.), and when the plant is burned, ashes are left containing the potassium, now in the form of carbonate. By washing such ashes (chiefly wood-ashes) with water and filtering, the insoluble matter (carbonates, phosphates, and sulphates of calcium and magnesium, silica, etc.) is left behind, whilst a lye is obtained containing the soluble constituents, of which potassium carbonate is the principal one, chlorides and sulphates of potassium and sodium also being present in small quantities.

By evaporation of this lye to dryness an impure potassium carbonate is obtained, which is sold as *crude potash.*

Up to within twenty-five years ago the chief supply of potash was obtained by this process, and the trees of thousands of acres were burned with the view of obtaining potash. To-day this mode of manufacturing potash is very limited, and is rapidly decreasing, as, fortunately, an almost unlimited supply of soluble potassium salts is furnished by the salt-mines of Stassfurt, Germany, where large quantities of potassium chloride (combined or mixed with the chlorides and sulphates of sodium, magnesium, calcium, and other salts) are found, from which the carbonate and other salts are manufactured.

Potassium hydroxide, Potassium hydrate, Potassa, KOH=56 (*Caustic potash*), may be obtained by the action of the metal on water:

$$K + H_2O = H + KOH.$$

The usual process for making potassium hydroxide is to boil together a dilute solution of potassium carbonate or bicarbonate and calcium hydroxide:

$$K_2CO_3 + Ca(OH)_2 = CaCO_3 + 2KOH.$$

Experiment 16. Add gradually 5 grammes of calcium hydroxide (slaked lime) to a boiling solution of about 5 grammes of potassium carbonate in 50 c.c. of water, and continue to boil until the conversion of potassium carbonate into hydroxide is complete. This can be shown by filtering off a few drops of the liquid, and supersaturating with dilute hydrochloric acid, which should not cause effervescence. Set aside to cool, and when all solids have subsided, pour off the clear solution of potassium hydroxide, which may be used for Experiment 17. What quantities of K_2CO_3 and $Ca(OH)_2$ are required to make one liter of a 5 per cent. solution of potassium hydroxide?

Potassium hydroxide is a white, hard, highly deliquescent substance, soluble in 0.5 part of water and 2 parts of alcohol; it fuses at a low red heat, forming an oily liquid, which may be poured into suitable moulds to form pencils; at a strong red heat it is slowly volatilized without decomposition; it is strongly alkaline and a powerful base, readily combining with all acids; it rapidly destroys organic tissues, and when taken internally acts as a powerful corrosive, and most likely otherwise as a poison

Antidotes: dilute acids, vinegar, to form salts; or fat, oil, or milk, to form soap.

Liquor potassæ is a 5 per cent. solution of potassium hydroxide in water.

Potassa with lime is a mixture of equal parts of potassium hydroxide and calcium oxide.

Potassium oxide, K_2O. This compound can be obtained either by burning potassium in air and subsequent heating of the product to a high temperature, or by fusing together potassium hydroxide and metallic potassium:

$$2KOH + 2K = 2K_2O + 2H$$

Besides this potassium monoxide, corresponding to water in its composition, two other oxides of the composition K_2O_2 (corresponding to hydrogen peroxide, H_2O_2) and K_2O_4 are known. The latter oxide is obtained by the combustion of potassium in oxygen. It is a strong oxidizing agent, and at a high temperature is decomposed into oxide and oxygen.

Potassium carbonate, Potassii carbonas, $K_2CO_3 = 138$, is obtained from wood-ashes in an impure state as described above, or from the native chloride by the so-called Leblanc process, which will be described in connection with sodium carbonate. Crude potash when calcined in a furnace until white is known as *pearlash.*

Pure potassium carbonate is obtained by heating the bicarbonate, which is decomposed as follows:

$$2KHCO_3 = K_2CO_3 + H_2O + CO_2.$$

Potassium carbonate is deliquescent, is soluble in about an equal weight of water, insoluble in alcohol, and has strong basic and alkaline properties.

Potassium bicarbonate, Potassii bicarbonas, $KHCO_3 = 100$. Obtained by passing carbon dioxide through a strong solution of potassium carbonate, when the less soluble bicarbonate forms and separates into crystals:

$$K_2CO_3 + H_2O + CO_2 = 2KHCO_3.$$

Potassium nitrate, Potassii nitras, $KNO_3 = 101$ (*Nitre, Saltpetre*). KnO_3
Potassium and sodium nitrate are found as an incrustation upon and throughout the soil of certain localities in dry and hot countries, as, for instance, in Peru, Chili, and India. The formation of these nitrates is to be explained by the absorption of ammonia by the soil, where it gradually is oxidized and converted into nitric acid. This nitrification, *i. e.*, the conversion of ammonia into nitric acid, seems to be due largely to the action of micro-organisms termed the nitrifying ferment. The acid after being formed combines with the strongest base present in the soil. If this base be potash, potassium nitrate will be formed; if soda, sodium nitrate; if lime, calcium nitrate.

Upon the same principle is based the manufacture of nitre on a large scale, which is accomplished by mixing animal refuse matter with earth and lime, and placing the mixture in heaps under a roof, to prevent lixiviation by rain. By decomposition (putrefaction) of the animal matter, ammonia is formed, which, by oxidation, is converted into nitric acid, which then combines with the calcium of the lime, forming calcium nitrate. This is dissolved in water, and to the solution potassium carbonate (or chloride) is added, when calcium carbonate (or chloride) and potassium nitrate are formed:

$$Ca(NO_3)_2 + K_2CO_3 = 2KNO_3 + CaCO_3$$

Large quantities of potassium nitrate are made also by decomposing sodium nitrate (Chili saltpetre) by potassium chloride:

$$NaNO_3 + KCl = KNO_3 + NaCl.$$

Potassium nitrate crystallizes in six-sided prisms; it is soluble in about 3.8 parts of cold, and 0.4 part of boiling water. It has a cooling, saline, and pungent taste, and a neutral reaction. When heated with deoxidizing agents or combustible substances, these are readily oxidized.

It is this oxidizing power which is made use of in the manufacture of *gunpowder*—an intimate mixture of potassium nitrate, sulphur, and carbon. Upon heating or igniting the gunpowder, the sulphur and carbon are oxidized, a considerable quantity of various gases (CO, CO_2, N, SO_2, etc.) being formed, the sudden generation and expansion of which cause the explosion.

Potassium chlorate, Potassii chloras, $KClO_3 = 122.4$ (*Chlorate of potassium*), may be obtained by the action of chlorine on a boiling solution of potassium hydroxide:

$$6Cl + 6KOH = 5KCl + KClO_3 + 3H_2O.$$

A cheaper process for the manufacture of potassium chlorate is the action of chlorine upon a boiling solution of potassium carbonate, to which calcium hydroxide has been added:

$$K_2CO_3 + 6(Ca2OH) + 12Cl = 2KClO_3 + CaCO_3 + 5CaCl_2 + 6H_2O.$$

Potassium chlorate crystallizes in white plates of a pearly lustre; it is soluble in 16.7 parts of cold, and 1.7 parts of boiling water. It is even a stronger oxidizing agent than potassium nitrate, for which reason care must be taken in mixing it with organic matter or other deoxidizing agents, or with strong acids, which will liberate chloric acid. When heated by itself, it is decomposed into potassium chloride and oxygen.

Potassium sulphate, Potassii sulphas, $K_2SO_4 = 174$. Obtained by the decomposition of potassium chloride, nitrate, or carbonate, by sulphuric acid:

$$2KCl + H_2SO_4 = 2HCl + K_2SO_4;$$
$$K_2CO_3 + H_2SO_4 = H_2O + CO_2 + K_2SO_4.$$

Potassium sulphate exists in small quantities in plants, and in nearly all animal tissues and fluids, more abundantly in urine.

Potassium hydrogen sulphate, bisulphate, or potassium acid sulphate, may be obtained by the action of one molecule of potassium chloride upon one molecule of sulphuric acid:

$$KCl + H_2SO_4 = HCl + KHSO_4.$$

Potassium sulphite. Obtained by the decomposition of potassium carbonate by sulphurous acid:

$$K_2CO_3 + H_2SO_3 = H_2O + CO_2 + K_2SO_3.$$

Potassa Sulphurata, U.S.P. (*Sulphurated potassa, Liver of sulphur, Hepar sulphuris*). A mixture of potassium sulphide, polysulphide, and thiosulphate. It is made by heating a mixture of one part of sulphur and two parts of potassium carbonate in a covered crucible, and pouring the fused mass on a marble slab:

$$3K_2CO_3 + 8S = K_2S_2O_3 + 2K_2S_3 + 3CO_2.$$

The freshly prepared substance has a liver-brown color, turning gradually to greenish yellow; it is very apt to absorb water and oxygen, both the sulphide and hyposulphite becoming oxidized, and finally converted into sulphates.

Potassium hypophosphite, Potassii hypophosphis, KPH_2O_2= 104, may be obtained by decomposing a solution of calcium hypophosphite by potassium carbonate:

$$Ca(PH_2O_2)_2 + K_2CO_3 = 2KPH_2O_2 + CaCO_3.$$

The filtered solution is evaporated at a very gentle heat, stirring constantly from the time it begins to thicken until a dry, granular salt is obtained, which is soluble in 0.6 part of cold and 0.3 part of boiling water.

Potassium iodide, Potassii iodidum, KI = 165.5 is made by the addition of iodine to a solution of potassium hydroxide until the dark-brown color no longer disappears:

$$6KOH + 6I = 5KI + KIO_3 + 3H_2O.$$

Iodide and iodate of potassium are formed, and may be separated by crystallization. A better method, however, is to boil to dryness the liquid containing both salts, and to heat the mass after having mixed it with some charcoal, in a crucible, when the iodate is converted into iodide:

$$KIO_3 + 3C = KI + 3CO.$$

Experiment 17. Add to a solution of about 3 grammes of potassium hydroxide in about 25 c.c. of water (or to the solution obtained by making Experiment 16) iodine until the brown color no longer disappears. (How much iodine will be needed for 3 grammes of KOH?) Evaporate the resulting solution (What does this solution contain now?) to dryness, mix the powdered mass with about 10 per cent. of powdered charcoal and heat the mixture in a crucible until slight deflagration has taken place. Dissolve the fluid mass in hot water, filter and set aside for crystallization; if too much water has been used for dissolving, the liquid must be concentrated by evaporation.

Potassium iodide forms colorless, cubical crystals, which are soluble in 0.5 part of boiling and 0.8 part of cold water, also soluble in 18 parts of alcohol, and 2.5 parts of glycerin. When heated it fuses, and at a bright-red heat is volatilized without decomposition.

Potassium bromide, Potassii bromidum, $KBr = 118.8$ may be obtained in a manner analogous to that given for potassium iodide, by the action of bromine upon potassium hydroxide, etc.

Or it may be made by the decomposition of a solution of ferrous bromide by potassium carbonate:

$$FeBr_2 + K_2CO_3 = 2KBr + FeCO_3.$$

Ferrous carbonate is precipitated, whilst potassium bromide remains in solution, from which it is obtained by crystallization.

Potassium salts of interest, which have not yet been mentioned, will be considered under the head of their respective acids. Some of these salts are potassium chromate and permanganate, and the salts formed from organic acids, such as potassium tartrate, acetate, etc.

Analytical reactions.

(Potassium chloride, KCl, or nitrate, KNO_3, may be used.)

1. To a solution of potassium chloride, or to any salt of potassium, after a few drops of hydrochloric acid have been mixed with it, add platinic chloride and some alcohol: a yellow crystalline precipitate falls, which is a double chloride of platinum and potassium, $PtCl_4(KCl)_2$.

$$2KCl + PtCl_4 = PtCl_4(KCl)_2;$$
$$2KNO_3 + 2HCl + PtCl_4 = PtCl_4(KCl)_2 + 2HNO_3.$$

The last formula shows the necessity of adding hydrochloric acid, which is not required in case potassium chloride is used. The addition of alcohol facilitates the precipitation of the double chloride of potassium and platinum, because it is less soluble in alcohol than in water.

2. To a neutral or slightly acid solution of a potassium salt add sodium cobaltic nitrite: a yellow precipitate of potassium cobaltic nitrite, $(KNO_2)_6.Co_2(NO_2)_6 + H_2O$, is produced. (The reaction is

not influenced by the presence of alkaline earths, earths, or metals of the iron group.)

3. Add to a concentrated solution of a neutral potassium salt a freshly prepared strong solution of tartaric acid: a white precipitate of potassium acid tartrate, $KHC_4H_4O_6$, is slowly formed. Addition of alcohol facilitates precipitation.

4. Potassium compounds color violet the flame of a Bunsen burner or of alcohol. The presence of sodium, which colors the flame intensely yellow, interferes with this test, as it masks the violet caused by potassium. The difficulty may be overcome by observing the flame through a blue glass or through a thin vessel filled with a solution of indigo. The yellow light is absorbed by the blue medium, while the violet light passes through and can be recognized.

5. All compounds of potassium are white (unless the acid has a coloring effect), soluble in water, and not volatile at a low red heat.

20. SODIUM (NATRIUM).

$Na^{i} = 23$.

Occurrence in nature. Sodium is found very widely diffused in small quantities through all soils. It occurs in large quantities in combination with chlorine, as rock-salt, or common salt, which forms considerable deposits in some regions, or is dissolved in spring waters, and is by them carried to the rivers, and finally to the ocean, which contains immense quantities of sodium chloride. It is found, also, as nitrate, silicate, etc.

Sodium chloride, Sodii chloridum, NaCl = 58.4 (*Common salt*). This is the most important of all sodium compounds, and also is the material from which the other compounds are directly or indirectly

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QUESTIONS.—181. How is potassium found in nature, and from what sources is the chief supply of potassium salts obtained? 182. What color have the salts of the alkali metals, and which are insoluble? 183. Mention two processes for making potassium hydroxide, and what are its properties? 184. Show by symbols the conversion of carbonate into bicarbonate of potassium. 185. Explain the principle of the manufacture of potassium nitrate, and what is the office of the latter in gunpowder? 186. How is potassium chlorate made, and what are its properties? 187. Give the processes for manufacturing iodide and bromide of potassium, both in words and symbols. 188. State the composition of potassium sulphate and sulphite. How can they be obtained? 189. What is sulphuret of potash? 190. Mention tests for potassium compounds.

obtained. Common table-salt frequently contains small quantities of calcium and magnesium chlorides, the presence of which causes absorption of moisture, as these compounds are hygroscopic, whilst pure sodium chloride is not.

In the animal system, sodium chloride is found in all parts, it being of great importance in aiding the absorption of albuminoid substances and the phenomena of osmose; also by furnishing, through decomposition, the hydrochloric acid of the gastric juice.

Sodium chloride is soluble in 2.8 parts of cold water, and in 2.5 parts of boiling water; almost insoluble in alcohol; it crystallizes in cubes and has a neutral reaction.

Sodium hydroxide, Sodium hydrate, Soda, $NaOH = 40$, may be obtained by the processes mentioned for potassium hydroxide, which compound it closely resembles in its chemical and most of its physical properties.

Solution of soda is a 5 per cent. solution of the hydroxide in water.

Sodium carbonate, Sodii carbonas, $Na_2CO_3.10H_2O = 286$ (*Washing soda, Sal sodæ*). This compound is~~, of all alkaline~~ substances~~, the one~~ manufactured in the largest quantities, being used in the manufacture of many highly important articles, as, for instance, soap, glass, etc.

Sodium carbonate is made, according to Leblanc's process, from the chloride by first converting it into sulphate (salt-cake) by the action of sulphuric acid:

$$2NaCl + H_2SO_4 = 2HCl + Na_2SO_4$$

The escaping vapors of hydrochloric acid are absorbed in water, and this liquid acid is used largely in the manufacture of bleaching-powder. The sodium sulphate is mixed with coal and limestone (calcium carbonate) and the mixture heated in reverberatory furnaces, when decomposition takes place, calcium sulphide, sodium carbonate, and carbonic oxide being formed:

$$Na_2SO_4 + 4C + CaCO_3 = CaS + Na_2CO_3 + 4CO$$

The resulting mass, known as *black-ash,* is washed with water, which dissolves the sodium carbonate, whilst calcium sulphide enters into combination with calcium oxide, thus forming an insoluble double compound of oxy-sulphide of calcium.

The liquid obtained by washing the black-ash, when evaporated to dryness, yields *crude sodium carbonate,* or "*soda ash;*" when this is dissolved and crystallized it takes up ten molecules of water, forming the ordinary washing soda.

Sodium carbonate is manufactured also by the so-called ammonia process, or the Solvay process. This depends on the decomposition of sodium chloride by ammonium bicarbonate under pressure, when sodium bicarbonate and ammonium chloride are formed, thus:

$$NaCl + NH_4HCO_3 = NH_4Cl + NaHCO_3.$$

The sodium acid carbonate thus obtained is converted into carbonate by heating:

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

The carbon dioxide obtained by this action is caused to act upon ammonia, liberated from the ammonium chloride, obtained as one of the products in the first reaction. Ammonium carbonate is thus regenerated and used in a subsequent operation for the decomposition of common salt.

Sodium carbonate has strong alkaline properties; it is soluble in 1.6 parts of cold water, and in much less water at higher temperatures; the crystals lose water on exposure to the air, falling into a white powder; heat facilitates the expulsion of the water of crystallization, and is applied in making the *dried sodium carbonate, Sodii carbonas exsiccatus* of the U. S. P., which should contain about 73 per cent. of anhydrous sodium carbonate.

Sodium bicarbonate, Sodii bicarbonas, $NaHCO_3$ = 84. Obtained, as stated in the previous paragraph, by the ammonia-soda process. It can also be made by passing carbon dioxide over sodium carbonate from which the larger portion of water of crystallization has been expelled:

$$Na_2CO_2 + H_2O + CO_2 = 2NaHCO_3.$$

It is a white powder, having a cooling, mildly saline taste, and a slightly alkaline reaction. Soluble in 11.3 parts of cold water, and insoluble in alcohol. It is decomposed by heat or by hot water into sodium carbonate, water, and carbon dioxide.

Sodium sulphate, Sodii sulphas, $Na_2SO_410H_2O$ = 322 (*Glauber's salt*). Made, as mentioned above, by the action of sulphuric acid on sodium chloride, dissolving the salt thus obtained in water, and crystallizing. Large, colorless, transparent crystals, rapidly efflorescing on exposure to air. Soluble in 2.8 parts of water at 15° C. (59° F.), in 0.25 part at 34° C. (93° F.), and in 0.47 part of boiling water.

Experiment 18. Dissolve about 10 grammes of crystallized sodium carbonate in 10 c.c. of hot water, add to this solution dilute sulphuric acid until all effervescence ceases and the reaction on litmus-paper is exactly neutral. Evaporate to about 20 c.c., and set aside for crystallization. Explain the action taking place, and state how much H_2SO_4, and how much of the diluted sulphuric acid, U. S. P., are needed for the decomposition of 10 grammes of crystallized sodium carbonate.

Sodium sulphite, Sodii sulphis, $Na_2SO_3.7H_2O = 252$. Sodium bisulphite, Sodii bisulphis, $NaHSO_3 = 104$. By saturating a cold solution of sodium carbonate with sulphur dioxide, sodium bisulphite is formed, and separates in opaque crystals:

$$Na_2CO_3 + 2SO_2 + H_2O = 2NaHSO_3 + CO_2.$$

If to the sodium bisulphite thus obtained a quantity of sodium carbonate be added, equal to that first employed, the normal salt is formed:

$$2NaHSO_3 + Na_2CO_3 = 2Na_2SO_3 + H_2O + CO_2$$

Sodium thiosulphate, Sodium hyposulphite, Sodii hyposulphis, $Na_2S_2O_3.5H_2O = 248$. Made by digesting a solution of sodium sulphite with powdered sulphur, when combination slowly takes place:

$$Na_2SO_3 + S = Na_2S_2O_3.$$

It is used under the name of "hypo" in photography to dissolve chloride, bromide, or iodide of silver.

Disodium hydrogen phosphate, Sodii phosphas, $Na_2HPO_4.12H_2O = 358$ (*Sodium phosphate*) is made from calcium phosphate by the action of sulphuric acid, which removes two-thirds of the calcium, forming calcium sulphate, while acid phosphate of calcium is formed and remains in solution:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + CaH_4(PO_4)_2.$$

The solution is filtered and sodium carbonate added, when calcium phosphate is precipitated, phosphate of sodium, carbon dioxide, and water being formed:

$$CaH_4(PO_4)_2 + Na_2CO_3 = CaHPO_4 + H_2O + CO_2 + Na_2HPO_4.$$

The filtered and evaporated solution yields crystals of sodium phosphate, which have a slightly alkaline reaction to litmus, but not to phenol-phtalein.

Experiment 19. Mix thoroughly 30 grammes of bone-ash with 10 c.c. of sulphuric acid, let stand for some hours, add 20 c.c. of water, and again set aside for some hours. Mix with 40 c.c. of water, heat to the boiling-point, and filter. The residue on the filter is chiefly calcium sulphate. To the hot filtrate of calcium acid phosphate add concentrated solution of sodium carbonate until a precipitate ceases to form and the liquid is faintly alkaline, filter, evaporate, and let crystallize.

When sodium phosphate is heated to a low red heat it loses water, and is converted into pyrophosphate, which, dissolved in hot water, and crystallized, forms the *sodium pyrophosphate*, $Na_4P_2O_7.10H_2O$ of the U. S. P.

The normal sodium phosphate, Na_3PO_4, is known also, but it is not a very stable compound, being acted upon even by the moisture and carbon dioxide of the air, with the formation of sodium carbonate and disodium hydrogen phosphate, thus:

$$2Na_3PO_4 + H_2O + CO_2 = 2Na_2HPO_4 + Na_2CO_3.$$

Sodium nitrate, Sodii nitras, $NaNO_3 = 85$ (*Chili saltpetre, Cubic nitre*). Found in nature, and is purified by crystallization. The crystals are transparent, deliquescent, and readily soluble.

Sodium nitrite, $NaNO_2$, is formed by heating the nitrate to a sufficiently high temperature to expel one-third of the oxygen; or, better, by treating the fused nitrate with metallic lead, which latter is converted into oxide. The sodium nitrite which is formed is dissolved and purified by crystallization.

Sodium borate, Sodii boras, $Na_2B_4O_7 + 10H_2O = 382.2$ (*Borax*). This salt occurs in Clear Lake, Nevada, and in several lakes in Asia. It is manufactured by adding sodium carbonate to the boric acid found in Tuscany, Italy. It forms colorless, transparent crystals, but is sold mostly in the form of a white powder. It is slightly efflorescent, is soluble in 16 parts of cold, and in 0.5 part of boiling water; insoluble in alcohol, but soluble in one part of glycerin at 80° C. (176° F.). When heated, borax puffs up, loses water of crystallization, and at red heat it melts, forming a colorless liquid which, on cooling, solidifies to a transparent mass, known as *fused borax*, or *borax glass*. Molten borax has the power to combine with metallic oxides, forming double borates, some of which have a characteristic color, for which reason borax is used in blow-pipe analysis. Borax has antiseptic properties, preventing the decomposition of some organic substances.

Other sodium salts which are official are *sodium hypophosphite*, $NaPH_2O_2 + H_2O$; *bromide*, $NaBr$; *iodide*, NaI; *chlorate*, $NaClO_3$. These salts may be obtained by processes analogous to those given for the corresponding potassium compounds.

Tests for sodium.

(Sodium chloride, NaCl, may be used.)

1. As all salts of sodium are soluble in water, we cannot precipitate this metal in the form of a compound by any of the common

reagents. (Potassium antimoniate precipitates neutral solution of sodium salts, but this test is not reliable.)

2. The chief reaction for sodium is the flame-test, compounds of sodium imparting to a colorless flame yellow color, which is very intense, brilliant, and luminous. A crystal of potassium dichromate appears colorless, and a paper coated with red mercuric iodide appears white, when illuminated by the yellow sodium flame. (The spectroscope shows a characteristic yellow line.)

3. Sodium compounds are white and are not volatile at or below a red heat.

Lithium, Li = 7. Found in nature in combination with silicic acid in a few rare minerals or as a chloride in some spring waters. Of inorganic salts, *lithium bromide* and *carbonate* are official. Hydroxide, carbonate, and phosphate of lithium are much less soluble than the corresponding compounds of potassium and sodium. Sodium phosphate added to a strong solution of a lithium salt produces, on boiling, a white precipitate of lithium phosphate, Li_3PO_4. Lithium compounds color the flame a beautiful crimson or carmine-red.

21. AMMONIUM.

NH4

$NH_4^{i} = 18$.

General remarks. The salts of ammonium show so much resemblance, both in their physical and chemical properties, to those of the alkali-metals, that they may be studied most conveniently at this place.

The compound radical NH_4 acts in these ammonium salts very much like one atom of an alkali-metal, and, therefore, frequently has been looked upon as a compound metal. The physical metallic properties (lustre, etc.) of ammonium cannot be fully demonstrated, as it is not capable of existing in a separate or free state. There is known, however, an alloy of ammonium and mercury, which may be obtained

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QUESTIONS.—191. What is the composition of common salt; how is it found in nature, and what is it used for? 192. Describe Leblanc's and the Solvay process for manufacturing sodium carbonate on a large scale. 193. How much water is in 100 pounds of the crystallized sodium carbonate? 194. What is Glauber salt, and how is it made? 195. State the composition of disodium hydrogen phosphate, and how is it prepared from calcium phosphate? 196. What difference exists between sodium carbonate and bicarbonate both in regard to physical and chemical properties? 197. Give the composition of sodium hyposulphite; what is it used for? 198. Which sodium salts are soluble, and which are insoluble? 199. How does sodium and how does lithium color the flame? 200. Which lithium salts are official?

by dissolving potassium in mercury, and adding to the potassium-amalgam thus formed, a strong solution of ammonium chloride, when potassium chloride and ammonium-amalgam are formed. The latter is a soft, spongy, metallic-looking substance, which readily decomposes into mercury, ammonia, and hydrogen:

$$HgK + NH_4Cl = KCl + NH_4Hg;$$
$$NH_4Hg = NH_3 + H + Hg.$$

The source of all ammonium compounds is ammonia NH_3, or ammonium hydroxide, NH_4OH, both of which have been considered heretofore.

Ammonium chloride, Ammonii chloridum, $NH_4Cl = 53.4$ (*Sal-ammoniac*). Obtained by saturating the "ammoniacal liquor" of the gas-works with hydrochloric acid, evaporating to dryness, and purifying the crude article by sublimation.

Pure ammonium chloride either is a white, crystalline powder, or occurs in the form of long, fibrous crystals, which are tough and flexible; it has a cooling, saline taste; is soluble in 3 parts of cold, and in 1 part of boiling water; and like all ammonium compounds, is completely volatilized by heat.

Experiment 20. To 10 c.c. of water of ammonia add hydrochloric acid until the solution is neutral to test paper. Evaporate to dryness and use the salt for the analytical reactions mentioned below. How many c.c. of 32 per cent. hydrochloric acid are required to saturate 10 c.c. of 10 per cent. ammonia water?

Ammonium carbonate, Ammonii carbonas, $NH_4HCO_3.NH_4NH_2CO_2 = 157$. Commercial ammonium carbonate is not the normal salt, but, as shown by the above formula, a combination of acid ammonium carbonate with ammonium carbamate. It is obtained by sublimation of a mixture of ammonium chloride and calcium carbonate, when calcium chloride is formed, ammonia gas and water escape, and ammonium carbonate condenses in the cooler part of the apparatus:

$$2CaCO_3 + 4NH_4Cl = NH_4HCO_3.NH_4NH_2CO_2 + 2CaCl_2 + H_2O + NH_3.$$

Ammonium carbonate thus obtained forms white, translucent masses, losing both ammonia and carbon dioxide on exposure to the air, becoming opaque, and finally converted into a white powder of acid ammonium carbonate.

$$NH_4HCO_3 NH_4NH_2CO_2 = NH_4HCO_3 + 2NH_3 + CO_2.$$

When commercial ammonium carbonate is dissolved in water the carbamate unites with one molecule of water, forming normal ammonium carbonate.

$$NH_4NH_2CO_2 + H_2O = (NH_4)_2CO_3.$$

A solution of the common ammonium carbonate in water is, consequently, a liquid containing both acid and normal carbonate of ammonium; by the addition of some ammonia water the acid carbonate is converted into the normal salt. The solution thus obtained is used frequently as a reagent.

The *Aromatic spirit of ammonia* (sal volatile) is a solution of normal ammonium carbonate in diluted alcohol to which some essential oils have been added.

Ammonium sulphate, $(NH_4)_2SO_4$, Ammonium nitrate, NH_4NO_3, and Ammonium phosphate, $(NH_4)_2HPO_4$, may be obtained by the addition of the respective acids to ammonia water or ammonium carbonate:

$$\begin{aligned} H_2SO_4 + 2NH_4OH &= (NH_4)_2SO_4 + 2H_2O. \\ HNO_3 + NH_4OH &= NH_4NO_3 + H_2O. \\ H_3PO_4 + 2NH_4OH &= (NH_4)_2HPO_4 + 2H_2O. \\ H_2SO_4 + (NH_4)_2CO_3 &= (NH_4)_2SO_4 + H_2O + CO_2. \end{aligned}$$

Ammonium iodide, Ammonii iodidum, NH_4I, and Ammonium bromide, Ammonii bromidum, NH_4Br, may be obtained by mixing together strong solutions of potassium iodide (or bromide) and ammonium sulphate, and adding alcohol, which precipitates the potassium sulphate formed; by evaporation of the solution the ammonium iodide (or bromide) is obtained:

$$\begin{aligned} 2KI + (NH_4)_2SO_4 &= 2NH_4I + K_2SO_4; \\ 2KBr + (NH_4)_2SO_4 &= 2NH_4Br + K_2SO_4. \end{aligned}$$

Another mode of preparing these compounds is by the decomposition of ferrous bromide (or iodide) by ammonium hydroxide:

$$FeBr_2 + 2NH_4OH = 2NH_4Br + Fe(OH)_2.$$

Ammonium iodide is the principal constituent of the *Decolorized tincture of iodine.*

Ammonium hydrogen sulphide, NH_4SH (*Ammonium hydrosulphide, Ammonium sulphydrate*). Obtained by passing hydrogen sulphide through water of ammonia until this is saturated:

$$H_2S + NH_4OH = NH_4SH + H_2O.$$

The solution thus obtained is, when recently prepared, a colorless liquid, having the odor of both ammonia and of hydrogen sulphide; when exposed to the air it soon assumes a yellow color. By the addition of ammonia water it is converted into *ammonium sulphide,* $(NH_4)_2S$:

$$NH_4SH + NH_4OH = (NH_4)_2S + H_2O.$$

Both substances, the ammonium hydrogen sulphide and ammonium sulphide, are valuable reagents, frequently used for precipitation of certain heavy metals, or for dissolving certain metallic sulphides.

Analytical reactions.

(Ammonium chloride, NH_4Cl, may be used.)

1. All compounds of ammonium are volatilized by heating to a low red heat.

2. All compounds of ammonium evolve ammonia gas when heated with hydroxide of calcium, potassium, or sodium. The ammonia may be recognized by its odor, or by its action on paper moistened with solution of cupric sulphate, which is thereby colored dark-blue, or by causing the appearance of dense white fumes of ammonium chloride, upon holding a glass rod, moistened with hydrochloric acid, in the gas.

3. Add to solution of ammonium salt some platinic chloride, a few drops of hydrochloric acid, and some alcohol; a yellow precipitate of ammonium platinic chloride, $(NH_4Cl)_2PtCl_4$, is produced. See explanation of the corresponding potassium reaction on page 140.

4. The addition of sodium cobaltic nitrite causes in neutral or acid solutions a yellow precipitate of ammonium cobaltic nitrite, $(NH_4NO_2)_6.Co_2.(NO_2)_6$.

5. Ammonium salts are colorless, and (almost all) soluble in water. Traces of ammonium compounds may be detected by alkaline mercuric-potassium iodide (Nessler's solution), which causes a reddish-brown precipitate or coloration.

Summary of analytical characters of the alkali-metals.

	Potassinm.	*Sodium.*	*Lithium.*	*Ammonium.*
Sodium cobaltic nitrite . .	Yellow precipitate.	....	....	Yellow precipitate.
Platinic chloride	Yellow precipitate.	....	....	Yellow precipitate.
Sodium bitartrate . . .	White precipitate.	....	....	White precipitate.
Sodium phosphate . . .	....	....	White precipitate in conc. solution on boiling.	....
Sodium hydroxide . . .	....	....	....	Ammonia gas.
Action of heat	Fusible.	Fusible.	Fusible.	Volatile.
Flame color	Violet.	Yellow.	Crimson.	....

Questions.—201. What is ammonium, and why is it classed with the alkali-metals? 202. Is ammonium known in a separate state? 203. What is ammonium-amalgam, how is it obtained, and what are its properties? 204. What is

22. MAGNESIUM.

$Mg^{ii} = 24.3.$

General remarks. Magnesium occupies a position intermediate between the alkali metals and the alkaline earths. To some extent it resembles also the heavy metal zinc, with which it has in common the volatility of the chloride, the solubility of the sulphate, and the isomorphism of several of its compounds with the analogously constituted compounds of zinc.

Occurrence in nature. Magnesium is widely diffused in nature, and several of its compounds are found in large quantities. It occurs as chloride and sulphate in many spring waters and in the salt-mines of Strassfurt; as carbonate in the mineral *magnesite;* as double carbonate of magnesium and calcium in the mineral *dolomite* (magnesian limestone), which forms entire mountains; as silicate of magnesium in the minerals *serpentine, meerschaum, talc, asbestos, soapstone,* etc.

Metallic magnesium may be obtained by the decomposition of magnesium chloride by sodium:

$$MgCl_2 + 2Na = 2NaCl + Mg.$$

Magnesium is an almost silver-white metal, losing its lustre rapidly in moist air by oxidation of the surface. It decomposes ~~hot water~~ with liberation of hydrogen:

$$Mg + 2H_2O = 2H + Mg(OH)_2.$$

When heated to a red heat it burns with a brilliant bluish-white light forming magnesium oxide.

Magnesium carbonate, Magnesii carbonas. Approximately: $(MgCO_3)_4.Mg(OH)_2.5H_2O$ (*Magnesia alba, Light magnesia*). The normal magnesium carbonate, $MgCO_3$, is found in nature, but the official preparation contains carbonate, hydroxide, and water. It is obtained by boiling a solution of magnesium sulphate with solution

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the source of ammonium compounds? 205. State the composition, mode of preparation, and properties of sal-ammoniac. 206. How is ammonium carbonate manufactured, and what difference exists between the solid article and its solution? 207. State the composition of ammonium sulphide and of ammonium hydrogen sulphide; how are they made, and what are they used for? 208. By what process may ammonium sulphate, nitrate, and phosphate be obtained from ammonium hydroxide or ammonium carbonate, and what chemical change takes place? 209. How does heat act upon ammonium compounds? 210. Give analytical reactions for ammonium salts.

of sodium carbonate, when the carbonate is precipitated, some carbon dioxide evolved, and sodium sulphate remains in solution:

$$5MgSO_4 + 5Na_2CO_3 + 6H_2O = (MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O + 5Na_2SO_4 + CO_2.$$

By filtering, washing, and drying the precipitate, it is obtained in the form of a white, light powder; if, however, the above-mentioned solutions are mixed, evaporated to dryness, and the sodium sulphate removed by washing, the magnesium carbonate is left in a more dense condition, and is then known as *heavy magnesium carbonate.*

Experiment 21. Dissolve 10 grammes of magnesium sulphate in hot water and add a concentrated solution of sodium carbonate until no more precipitate is formed. Collect the precipitated magnesium carbonate on a filter and dry it at a low temperature. (How much crystallized sodium carbonate is needed for the decomposition of 10 grammes of crystallized magnesium sulphate?) Notice that the dried precipitate evolves carbon dioxide when heated with acids.

Magnesium oxide, Magnesia, MgO = 40.3 (*Calcined magnesia, Light magnesia*), is obtained by heating light magnesium carbonate in a crucible to a full red heat, when all carbon dioxide and water are expelled:

$$(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O = 5MgO + 4CO_2 + 6H_2O.$$

It is a very light, amorphous, white, almost tasteless powder, which absorbs moisture and carbon dioxide gradually from the air; in contact with water it forms the hydroxide $Mg(OH)_2$, which is almost insoluble in water, requiring of the latter over 50,000 parts for solution. Milk of magnesia is the hydroxide suspended in water (1 part in about 15).

The *heavy magnesia, magnesia ponderosa* of the U. S. P., differs from the common or light magnesia, not in its chemical composition, but merely in its physical condition, being a white, dense powder obtained by heating the heavy magnesium carbonate.

Experiment 22. Place 1 gramme of magnesium carbonate, obtained in performing Experiment 21, into a weighed crucible and heat to redness, or until by further heating no more loss in weight ensues. Treat the residue with dilute hydrochloric acid and notice that no evolution of carbon dioxide takes place. What is the calculated loss in weight of magnesium carbonate when converted into oxide, and how does this correspond with the actual loss determined by the experiment?

Magnesium sulphate, Magnesii sulphas, $MgSO_4.7H_2O$ = 246.3 (*Epsom salt*), is obtained from spring waters, from the mineral

Kieserite, $MgSo_4.H_2O$, and by decomposition of the native carbonate by sulphuric acid:

$$MgCO_3 + H_2SO_4 = MgSO_4 + CO_2 + H_2O.$$

It forms colorless crystals, which have a cooling, saline, and bitter taste, a neutral reaction, and are easily soluble in water.

Analytical reactions.

(Magnesium sulphate, $MgSO_4$, may be used.)

1. Add to a magnesium solution potassium or sodium carbonate and heat: a white precipitate of basic magnesium carbonate, $4MgCO_3.Mg(OH)_2$, is produced.

2. Add to a magnesium solution ammonium carbonate (or ammonium hydroxide): part of the magnesium will be precipitated as carbonate (or hydroxide). These precipitates, however, are soluble in ammonium chloride and many other ammonium salts: if these latter had been added previously to the magnesium solution, ammonium carbonate (or hydroxide) would cause no precipitation. (The dissolving action of the ammonium chloride is due to the tendency of magnesium to form double salts with ammonium salts.)

3. To solution of magnesium add a solution containing sodium phosphate, ammonium chloride, and ammonia: a white crystalline precipitate of magnesium ammonium phosphate, $MgNH_4PO_4$, is produced, which is somewhat soluble in water, but almost insoluble in water containing some ammonia.

4. Salts of magnesium are white and soluble, except the carbonate, phosphate, and arsenate; the oxide and hydroxide also are insoluble; the latter is precipitated by sodium or potassium hydroxide.

23. CALCIUM.

$Ca^{ii} = 40\ (39.91)$.

General remarks regarding the metals of the alkaline earths. The three metals, calcium, barium, and strontium, form the second

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QUESTIONS.—211. How is magnesium found in nature? 212. By what process is metallic magnesium obtained? 213. Give the physical and chemical properties of magnesium. 214. State two methods by which magnesium oxide can be obtained. 215. What is calcined magnesia? 216. State the composition and properties of the official magnesium carbonate, and how it is made. 217. What is Epsom salt, and how is it obtained? 218. Which compounds of magnesium are insoluble? 219. Give tests for magnesium compounds. 220. How can the presence of magnesium be demonstrated in a mixture of magnesium sulphate and sodium sulphate?

group of light metals. Similar to the alkali-metals, they decompose water at the ordinary temperature with liberation of hydrogen; their separation in the elementary state is even more difficult than that of the alkali-metals.

They differ from the latter by forming insoluble carbonates and phosphates (those of the alkalies are soluble), from the earths by their soluble hydroxides (those of the earths are insoluble), and from all heavy metals by the solubility of their sulphides (those of heavy metals are insoluble). The sulphates are either insoluble (barium) or sparingly soluble (strontium and calcium). The hydroxides and carbonates are decomposed by heat, water or carbon dioxide being expelled and the oxides formed. In case of calcium carbonate this decomposition takes place easily, while the carbonates of barium and strontium require a much higher temperature. They are bivalent elements.

Occurrence in nature. Calcium is one of the most abundantly occurring elements. As carbonate ($CaCO_3$) it is found in the form of calc-spar, limestone, chalk, marble, shells of eggs and mollusca, etc., or, as acid carbonate, dissolved in water. The sulphate is found as *gypsum* or *alabaster*, $CaSO_42H_2O$; the phosphate, $Ca_3(PO_4)_2$, in the different phosphatic rocks (apatite, etc.); the fluoride, CaF_2, as fluor-spar; the chloride, $CaCl_2$, in some waters, and the silicate in many rocks. It enters the vegetable and animal system in various forms of combination, chiefly, however, as phosphate and sulphate.

Calcium oxide, Lime, Calx, CaO = 56 (*Quick-lime, Burned lime*), is obtained on a large scale by the common process of lime-burning, which is the heating of limestone or any other calcium carbonate to about 800° C. (1472° F.), in furnaces termed lime-kilns. On a small scale decomposition may be accomplished in a suitable crucible over a blowpipe flame:

$$CaCO_3 = CaO + CO_2.$$

The pieces of oxide thus formed retain the shape and size of the carbonate used for decomposition.

Lime is a white, odorless, amorphous, infusible substance, of alkaline taste and reaction; exposed to the air it gradually absorbs moisture and carbon dioxide, the mixture thus formed being known as air-slaked lime.

Lime occupies among bases a position similar to that of sulphuric acid among acids, and is used directly or indirectly in many branches of chemical manufacture.

Calcium hydroxide, Calcium hydrate, $Ca(OH)_2$ (*Slaked lime*). When water is sprinkled upon pieces of calcium oxide, the two substances combine chemically, liberating much heat; the pieces swell up, and are converted gradually into a dry, white powder, which is the *slaked lime.* When this is mixed with water, the so-called *milk of lime* is formed.

Lime-water, Liquor calcis (*Solution of lime*). This is a saturated solution of calcium hydroxide in water: 10,000 parts of the latter dissolving about 15 to 17 parts of hydroxide. In making lime-water, 1 part of calcium oxide is slaked and agitated occasionally during half an hour with 30 parts of water. The mixture is then allowed to settle, and the liquid, containing besides calcium hydroxide the salts of the alkali-metals which may have been present in the lime, is decanted and thrown away. To the calcium hydroxide left, and thus purified, 300 parts of water are added and occasionally shaken in a well-stoppered bottle, from which the clear liquid may be poured off for use.

Lime-water is a colorless, odorless liquid, having a feebly caustic taste and an alkaline reaction. When heated to boiling it becomes turbid by precipitation of calcium hydroxide (or perhaps oxide) which re-dissolves when the liquid is cooled. Carbon dioxide causes a precipitation of calcium carbonate.

Experiment 23. Make lime-water according to directions given above.

Calcium carbonate, Calcii carbonas præcipitatus, $CaCO_3$ = 100. Precipitated calcium carbonate is obtained as a white, tasteless, neutral, impalpuble powder by mixing solutions of calcium chloride and sodium carbonate:

$$CaCl_2 + Na_2CO_3 = 2NaCl + CaCO_3.$$

Experiment 24. Add to about 10 grammes of marble (calcium carbonate) in small pieces, hydrochloric acid as long as effervescence takes place; filter the solution of calcium chloride thus obtained and add to it solution of sodium carbonate as long as a precipitate is formed, collect the precipitate on a filter, wash and dry it.

Calcium sulphate, $CaSO_4$ = 136 (*Dried gypsum, Plaster-of-Paris, Calcined plaster*). It has been mentioned above that the mineral *gypsum* is native calcium sulphate in combination with 2 molecules of water of crystallization. By heating to about 115° C. (239° F.) most of this water is expelled, and a nearly anhydrous sulphate formed. This article readily recombines with water, becoming a hard mass, for which reason it is used for making moulds and casts, and in surgery. If the gypsum is heated to a considerably higher temperature than the one mentioned, all water is expelled, and the product thus obtained combines with water but very slowly.

Tricalcium phosphate, Calcii phosphas præcipitatus, $Ca_3(PO_4)_2 = 310$ (*Precipitated calcium phosphate, Phosphate of lime, Bone-phosphate*). By dissolving bone-ash (bone from which all organic matter has been expelled by heat) in hydrochloric acid, and precipitating the solution with ammonia water there is obtained calcium phosphate, which contains traces of calcium fluoride and magnesium phosphate.

A pure article is made by precipitating a solution of calcium chloride by sodium phosphate and ammonia:

$$2Na_2HPO_4 + 3CaCl_2 + 2NH_4OH = Ca_3(PO_4)_2 + 4NaCl + 2NH_4Cl + 2H_2O.$$

It is a white, tasteless, amorphous powder, insoluble in cold water, soluble in hydrochloric or nitric acids.

Superphosphate, or acid phosphate of lime. Among the inorganic substances which serve as plant-food, calcium phosphate is a highly important one. As this compound is found usually in very small quantities as a constituent of the soil, and as this small quantity is soon removed by the various crops taken from a cultivated soil, it becomes necessary to replace it in order to enable the plant to grow and to form seeds.

For this purpose the various phosphatic rocks (chiefly calcium phosphate) are converted into commercial fertilizers, which is accomplished by the addition of sulphuric acid to the ground rock. The sulphuric acid removes from the tricalcium phosphate one or two atoms of calcium, forming mono- or dicalcium phosphate and calcium sulphate. The mixture of these substances, containing also the impurities originally present in the phosphatic rocks, is sold as acid phosphate or superphosphate.

Bone-black and bone-ash. Phosphates enter the animal system in the various kinds of food, and are to be found in every tissue and fluid, but most abundantly in the bones and teeth. Bones contain about 30 per cent. of organic and 70 per cent. of inorganic matter, most of which is tricalcium phosphate. When bones are burned until all the organic matter has been destroyed and volatilized, the resulting product is known as *bone-ash*. If, however, the bones are subjected to the process of destructive distillation (heating with exclusion of air), the organic matter suffers decomposition, many volatile products escape, and most of the non-volatile carbon remains mixed with the inorganic portion of the bones, which substance is known as *bone-black* or *animal charcoal.*

Calcium hypophosphite, Calcii hypophosphis, $Ca(PH_2O_2)_2 =$ 170. Obtained by heating pieces of phosphorus with milk of lime until hydrogen phosphide ceases to escape. From the filtered liquid the excess of lime is removed by carbon dioxide, and the clear liquid evaporated to dryness. (Great care must be taken during the whole of the operation, which is somewhat dangerous on account of the inflammable and explosive nature of the compounds.)

$$8P + 6H_2O + 3[Ca(OH)_2] = 3[Ca(PH_2O_2)_2] + 2PH_3.$$

Calcium hypophosphite is generally met with as a white, crystalline powder with a pearly lustre; it is soluble in 6 parts of water and has a neutral reaction to litmus.

Calcium chloride, Calcii chloridum, $CaCl_2 = 110.8$, and **Calcium bromide, Calcii bromidum, $CaBr_2 = 199.6$,** may both be obtained by dissolving calcium carbonate in hydrochloric acid or hydrobromic acid, until the acids are neutralized. Both salts are highly deliquescent.

Chlorinated lime, Calx chlorata (*Bleaching-powder*, incorrectly called *Chloride of lime*). This is chiefly a mixture (according to some, a compound) of calcium chloride with calcium hypochlorite, and is manufactured on a very large scale by the action of chlorine upon calcium hydroxide:

$$\underset{\text{Calcium hydroxide.}}{2Ca(OH)_2} + 4Cl = 2H_2O + \underbrace{Ca(ClO)_2 + CaCl_2}_{\text{Chlorinated lime.}}.$$

Bleaching-powder is a white powder, having a feeble chlorine-like odor; exposed to the air it becomes damp from absorption of moisture, undergoing decomposition at the same time; with dilute acids it evolves chlorine, of which it should contain not less than 35 per cent. in available form. The action of hydrochloric acid takes place thus:

$$Ca(ClO)_2 + 2HCl = CaCl_2 + 2HClO;$$
$$2HClO + 2HCl = 2H_2O + 4Cl.$$

Bleaching-powder is a powerful disinfecting and bleaching agent.

Sulphurated lime, Calx sulphurata, is a mixture of calcium sulphide and sulphate, obtained by heating to redness in a crucible a mixture of dried calcium sulphate, starch, and charcoal until the contents have lost their black color. By the deoxidizing action of coal and starch the larger portion of calcium sulphate is converted into sulphide.

Analytical reactions.

(Calcium chloride, $CaCl_2$, may be used.)

1. Add to solution of a calcium salt, the carbonate of either potassium, sodium, or ammonium: a white precipitate of calcium carbonate, $CaCO_3$, is produced.
2. Add sodium phosphate to neutral solution of calcium: a white precipitate of calcium phosphate, $CaHPO_4$, is produced.
3. Add ammonium (or potassium) oxalate to a calcium solution: a white precipitate of calcium oxalate, CaC_2O_4, is produced, which is insoluble in acetic, soluble in hydrochloric acid.
4. Sulphuric acid or soluble sulphates produce a white precipitate of calcium sulphate, $CaSO_4$, in concentrated, but not in dilute solutions of calcium.
5. Add potassium or sodium hydroxide: a white precipitate of calcium hydroxide, $Ca(OH)_2$, is produced in concentrated, but not in diluted solutions. Ammonia water gives no precipitate.
6. Calcium compounds impart a reddish-yellow color to the flame.

Stontium, $Sr^{ii} = 87.3$. Found in a few localities in the minerals *strontianite*, $SrCO_3$, and *celestite*, $SrSO_4$. Its compounds resemble those of calcium and barium. The *oxide*, SrO, cannot be obtained easily by heating the carbonate, as this is much more stable than calcium carbonate. It may, however, be readily prepared by heating the nitrate. The *hydroxide*, $Sr(OH)_2$, is formed when the oxide is brought in contact with water; it is more soluble than calcium hydroxide.

Strontium nitrate, $Sr(NO_3)_2$, *Strontium chloride*, $SrCl_2$, *Strontium bromide*, $SrBr_2$, and *Strontium iodide*, SrI_2, may be obtained by dissolving the carbonate in the respective acids. The nitrate is used extensively for pyrotechnic purposes, as strontium imparts a beautiful red color to flames; the bromide and iodide are official.

Analytical reactions.

(Strontium nitrate, $Sr(NO_3)_2$, may be used.)

1. The reactions of strontium with soluble carbonates, oxalates, and phosphates are analogous to those of calcium.

2. Add calcium sulphate: a white precipitate of strontium sulphate, $SrSO_4$, is formed after a few minutes.

3. Add sulphuric acid or a soluble sulphate: a white precipitate forms at once in concentrated, after a while in dilute solutions.

4. Add potassium chromate; a pale-yellow precipitate of strontium chromate, $SrCrO_4$, is formed, which is soluble in acetic acid and in hydrochloric acid. (Potassium dichromate causes no precipitation.)

5. Strontium compounds color the flame beautifully red.

Barium, $Ba^{ii} = 136.9$. Occurs in nature chiefly as sulphate in *barite* or *heavy spar*, $BaSO_4$, but also as carbonate in *witherite*, $BaCO_3$. Barium and its compounds resemble closely those of calcium and strontium.

Barium chloride, $BaCl_2 + 2H_2O$, is prepared by dissolving the carbonate in hydrochloric acid. It crystallizes in prismatic plates, and is used as a valuable reagent.

Barium dioxide or peroxide, BaO_2, is made by heating the oxide to a dark-red heat in the air or in oxygen. When heated above the temperature at which it is formed, decomposition into oxide and oxygen takes place. This power to absorb oxygen from air and to give it up again at a higher temperature has been used as a method of preparing oxygen on the large scale. Unfortunately, the barium oxide cannot be used for an unlimited number of operations, as it loses the power to absorb oxygen after it has been heated several times. The use made of barium dioxide in preparing hydrogen dioxide has been mentioned before.

Barium dioxide is a heavy, grayish-white, amorphous powder, almost insoluble in water, with which, however, it forms a hydroxide, and to which it imparts an alkaline reaction.

Barium oxide, BaO, is made by heating *barium nitrate*, $Ba(NO_3)_2$, which itself is made by dissolving *barium carbonate* in nitric acid.

Barium salts are poisonous; antidotes are sodium and magnesium sulphate.

Analytical reactions.

(Barium chloride, $BaCl_2$, may be used.)

1. The reactions of strontium with soluble carbonates, oxalates, and phosphates are analogous to those of calcium solutions.

2. Add sulphuric acid or soluble sulphates: a white precipitate of barium sulphate, $BaSo_4$, is produced immediately, even in dilute solutions. The precipitate is insoluble in all diluted acids.

3. Add calcium sulphate: a white precipitate, insoluble in all diluted acids, is formed immediately.

4. Add potassium chromate or dichromate: a pale-yellow precipitate of barium chromate, $BaCrO_4$, is formed, which is soluble in hydrochloric acid.

5. Barium compounds color the flame yellowish-green.

Summary of analytical characters of the alkaline earth-metals.

	Magnesium.	*Calcium.*	*Strontium.*	*Barium.*
Potassium dichromate . .	....	....	....	Yellow precipitate.
Potassium chromate . . .	....	....	Yellow precipitate.	Yellow precipitate
Calcium sulphate	....	....	White precipitate forming slowly	White precipitate forming at once.
Ammonium carbonate . .	White precipitate soluble in NH_4Cl.	White precipitate.	White precipitate.	White precipitate.
Ammonium hydroxide . .	White precipitate	....	....	....
Ammonium oxalate . . .	No precipitate unless very concentrated	White precipitate in dilute solution	White precipitate in strong solution.	White precipitate in strong solution.
Sodium phosphate . . .	White precipitate.	White precipitate.	White precipitate.	White precipitate
Flame color	....	Yellowish-red.	Red.	Yellowish-green.

24. ALUMINUM.

Al^{iii} 27 (27.04).

Aluminum is the representative of the metals of the earths proper; all other members of this class are found in nature in very small

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QUESTIONS.—221. Which metals form the group of the alkaline earths, and in what respect do their compounds differ from those of the alkali-metals? 222. How is calcium found in nature? 223. What is burned lime; from what, and by what process is it made, and how does water act on it? 224. What is lime-water; how is it made, and what are its properties? 225. Mention some varieties of calcium carbonate as found in nature, and how is it obtained by an artificial process from the chloride? 226. What is Plaster-of-Paris, and what is gypsum; what are they uesd for? 227. State composition and mode of manufacturing bleaching-powder; what are its properties, and how do acids act upon it? 228. What is bone-black, bone-ash, acid phosphate, and precipitated tricalcium phosphate? How are they made? 229. Give tests for barium, calcium and strontium; how can they be distinguished from each other? 230. Which compounds of barium and strontium are of interest, and what are they used for?

quantities, and are chiefly of scientific interest, with the exception of cerium, which furnishes an official preparation.

Occurrence in nature. Aluminum is found almost exclusively in the solid mineral portion of the earth; rarely more than traces of aluminum compounds are found dissolved in water, and the occurrence of aluminum in either the vegetable or animal organism seems to be purely accidental.

By far the largest quantity of aluminum is found in combination with silicic acid in the various silicated rocks forming the greater mass of our earth, such as feldspar, slate, basalt, granite, mica, hornblende, etc., or in the various modifications of clay formed by their decomposition.

The minerals known as *corundum*, *ruby*, *sapphire*, and *emery*, are aluminum oxide in a crystallized state, and more or less colored by traces of other substances.

Metallic aluminum may be obtained by the decomposition of aluminum chloride by metallic sodium:

$$Al_2Cl_6 + 6Na = 6NaCl + 2Al.$$

It is now manufactured by the electrolysis of aluminum and sodium fluoride.

Aluminum is an almost silver~~-white~~ metal of a very low specific gravity (2.67); it is capable of assuming a high polish, and for this reason is used for ornamental articles; it is very strong, yet malleable, and does not change in dry or moist air.

Some of the alloys of aluminum are now used in the arts, as, for instance, aluminum-bronze, an alloy resembling gold and composed of 10 parts of aluminum with 90 of copper.

Aluminum is trivalent, and shows, like a number of other elements (iron, chromium, etc.), the peculiarity that the double atom Al_2^{vi} acts as a single sexivalent atom.

Alum is the general name for a group of isomorphous salts, composed of one molecule of the sulphate of a univalent metal in combination with one molecule of the sulphate of a trivalent metal, combined in crystallizing with 24 molecules of water. The general formula of an alum is consequently $M^{i}_2SO_4M^{iii}_2(SO_4)_3.24H_2O$ or $M^{i}_2M^{iii}_2(SO_4)_4.24H_2O$. M^{i} represents in this case a univalent, M^{iii} a trivalent metal.

Alums known are, for instance:

Potassium-aluminum sulphate,	$K_2SO_4, Al_2(SO_4)_3.24H_2O$.
Ammonium-aluminum sulphate,	$(NH_4)_2SO_4, Al_2(SO_4)_3.24H_2O$.
Potassium-chromium sulphate,	$K_2SO_4, Cr_2(SO_4)_3.24H_2O$.
Ammonium-ferric sulphate,	$(NH_4)_2SO_4, Fe_2(SO_4)_3.24H_2O$.

The official *alum, alumen,* is the *potassium alum,* a white substance crystallizing in large octahedrons, soluble in 10 parts of cold and 0.3 part of boiling water; this solution has an acid reaction and a sweetish astringent taste.

Alum is manufactured on a large scale by decomposing certain kinds of clay (aluminum silicates) by sulphuric acid, when aluminum sulphate is formed, to the solution of which potassium or ammonium sulphate is added, when, on evaporation, potassium or ammonium alum crystallizes.

Dried alum, Alumen exsiccatum, $K_2SO_4.Al_2(SO_4)_3 = 516$. (*Burnt alum.*) This is common alum, from which the water of crystallization has been expelled by heat. It is a white powder, dissolving very slowly in cold, but quickly in boiling water.

Aluminum hydroxide, $Al_2(OH)_6 = 156$. Obtained by adding water of ammonia or solution of sodium carbonate to solution of alum, when aluminum hydroxide is precipitated in the form of a highly gelatinous substance, which, after being well washed, is dried at a temperature not exceeding 40° C. (104° F.).

$$K_2SO_4.Al_2(SO_4)_3 + 6NH_4OH = K_2SO_4 + 3[(NH_4)_2SO_4] + Al_2(OH)_6;$$
$$K_2SO_4Al_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = K_2SO_4 + 3Na_2SO_4 + 3CO_2 + Al_2(OH)_6.$$

The usual decomposition between a soluble carbonate and any soluble salt (provided decomposition takes place at all) is the formation of an insoluble carbonate; according to this rule, the addition of a soluble carbonate to alum should produce aluminum carbonate. The basic properties of aluminum oxide, however, are so weak that it is not capable of uniting with so weak an acid as carbonic acid, and it is for this reason that the decomposition takes place as shown by the above formula, with liberation of carbon dioxide, whilst the hydroxide is formed. (Other metals, the oxides of which have weak basic properties, show similar reactions, as, for instance, chromium, and iron in the ferric salts.)

The weak basic properties of aluminum are shown also by the fact that aluminum sulphate, chloride, and nitrate, and even alum itself, have an acid reaction, while the corresponding salts of the alkalies or alkaline earths are neutral.

Aluminum hydroxide shows considerable surface-attraction toward many substances, which property is made use of in the art of dyeing, where the hydroxide is used for retaining coloring matter upon the cotton-fibre. Practically this is accomplished by precipitating aluminum hydroxide from solutions containing coloring matter, which latter is carried down and precipitated upon the fibre by the aluminum hydroxide; or by impregnating the articles to be dyed with this compound and placing them in the colored solutions.

Experiment 25. Dissolve 10 grammes of sodium carbonate in 100 c.c. of water, heat it to boiling, and add to it, with constant stirring, a hot solution, made by dissolving 10 grammes of alum in 100 c.c. of water. Wash the precipitate first by decantation, and then upon a filter, until the washings are not rendered turbid by barium chloride. Dry a portion of the precipitate at a low temperature, and use as aluminum hydroxide. Mix a small quantity of the wet precipitate with a decoction of logwood (made by boiling about 0.2 grammes of logwood with 50 c.c. of water), agitate for a few minutes, and filter. Notice that the red color of the solution has entirely disappeared, or nearly so, in consequence of the great surface-attraction of the aluminum hydroxide for coloring matter.

Aluminum oxide, Al_2O_3 (*Alumina*), is obtained as a white, tasteless powder either by burning the metal or by expelling the water from the hydroxide by heat:

$$Al_2(OH)_6 = Al_2O_3 + 3H_2O.$$

Aluminum sulphate, Alumini sulphas, $Al_2(SO_4)_3.16H_2O=630$. A white crystalline powder, soluble in about its weight of water, obtained by dissolving the oxide or hydroxide in sulphuric acid and evaporating the solution to dryness over a water-bath.

$$Al_2(OH)_6 + 3H_2SO_4 = Al_2(SO_4)_3 + 6H_2O.$$

Aluminum chloride, Al_2Cl_6. This compound is of interest on account of being the salt from which the metal was formerly obtained. Most chlorides may be obtained by dissolving the metal, its oxide, hydroxide, or carbonate in hydrochloric acid. Accordingly aluminum chloride may be obtained in solution:

$$Al_2(OH)_6 + 6HCl = Al_2Cl_6 + 6H_2O.$$

On evaporating the solution to dryness, however, and heating the dry mass further with the view of expelling all water, decomposition takes place, hydrochloric acid escapes, and aluminum oxide is left:

$$Al_2Cl_6 + 3H_2O = Al_2O_3 + 6HCl.$$

Aluminum chloride, consequently, cannot be obtained in a pure state (free from water) by this process, but it may be made by exposing to the action of chlorine a heated mixture of aluminum oxide and carbon. Neither carbon nor chlorine alone causes any decomposition of the aluminum oxide, but by the united efforts of these two substances decomposition is accomplished:

$$Al_2O_3 + 3C + 6Cl = 3CO + Al_2Cl_6.$$

Clay is the name applied to a large class of mineral substances, differing considerably in composition, but possessing in common the two characteristic features of plasticity and the predominance of aluminum silicate in combination with water.

The various kinds of clay have been formed in the course of time from such double silicates as feldspar and others, by a process which is partly of a mechanical, partly of a chemical nature, and consists chiefly in the disintegration of rocks and a removal of potassium and sodium by the chemical action of carbonic acid, water, and other agents.

The various kinds of clay are used in the manufacture of *bricks, earthenware, stoneware, porcelain,* etc. The process of burning these substances accomplishes the hardening by expelling water which is present in the clay. Pure clay is white; the red color of the common varieties is due to the presence of ferric oxide. For china or porcelain, clay is used containing silicates of the alkalies which, in burning, melt, causing the production of a more homogoneous mass, while in common earthenware the pores, produced by expelling the moisture, remain unfilled.

Glass is similar in composition to the better varieties of porcelain. All varieties of glass are mixtures of fusible, insoluble silicates, made by fusing silicic acid (white sand) with different metallic oxides or carbonates, the silicic acid combining chemically with the metals. Sodium and calcium are the chief metals in common glass, though potassium, lead, and others also are frequently used. Color is imparted to the glass by the addition of certain metallic oxides, which have a coloring effect, as, for instance, manganese violet, cobalt blue, chromium green, etc.

Ultramarine is a beautiful blue substance, found in nature as the mineral "*lapis lazuli,*" which was highly valued by artists as a color before the discovery of the artificial process for manufacturing it.

Ultramarine is now manufactured on a very large scale by heating a mixture of clay, sodium sulphate and carbonate, sulphur, and charcoal in large crucibles, when decomposition takes place and the beautiful blue compound is obtained. As neither of the substances used in the manufacture has a tendency to form colored compounds, the formation of this blue ultramarine is rather surprising, and the true chemical constitution of it is yet unknown.

Ultramarine is insoluble in water and is decomposed by acids with liberation of hydrogen sulphide, which shows the presence of sodium sulphide. A green ultramarine is now also manufactured.

Analytical reactions.

(A solution of aluminum sulphate, $Al_2(SO_4)_3$, or of aluminum chloride, Al_2Cl_6, may be used.)

1. To solution of an aluminum salt add potassium or sodium hydroxide: a white gelatinous precipitate of aluminum hydroxide, $Al_2(OH)_6$, is produced, which is soluble in excess of the alkali.

2. To aluminum solution add ammonium hydroxide: the same precipitate as above is obtained, but it is insoluble in an excess of the reagent.

3. The carbonates of ammonium, sodium, or potassium produce the same precipitate with liberation of carbon dioxide. (See explanation above.)

4. Ammonium sulphide produces the same precipitate with liberation of hydrogen sulphide:

$$Al_2Cl_6 + 3(NH_4)_2S + 6H_2O = Al_2(OH)_6 + 6NH_4Cl + 3H_2S.$$

5. Sodium phosphate produces a precipitate of aluminum phosphate, soluble in acids.

Cerium, Ce = 141. This element occurs in nature sparingly in a few rare minerals, chiefly as silicate in *cerite*. In its general deportment cerium resembles aluminum. Cerous solutions give with either ammonium sulphide, or ammonium and sodium hydroxide, a white precipitate of cerous hydroxide, $Ce_2(OH)_6$. Ammonium oxalate forms a white precipitate of *cerous oxalate*, $Ce_2(C_2O_4)_39H_2O$, which is the only official cerium preparation. Cerium oxalate is a white, granular powder, insoluble in water and alcohol, but soluble in hydrochloric acid. Exposed to a red heat it is decomposed and converted into reddish-yellow ceric oxide. If this oxide, or the residue obtained by heating any cerium salt to red heat, is dissolved in concentrated sulphuric acid, and a crystal of strychnine added, a deep blue color appears, which changes first to purple and then to red.

QUESTIONS.—231. Mention some varieties of crystallized aluminum oxide found in nature and some silicates containing it. 232. Give the general formula of an alum, and mention some alums. 233. Which alum is official, how is it made, what are its properties, and what is it used for? 234. What is dried alum, and how does it differ from common alum? 235. How is aluminum chloride made, and how is the metal obtained from it? 236. State the properties of aluminum. 237. What change takes place when ammonium hydroxide, and what change when sodium carbonate is added to a solution of alum? 238. What is the composition of earthenware, porcelain, and glass; how and from what materials are they manufactured? 239. What is ultramarine? 240. Give tests for aluminum compounds.

Summary of analytical characters of the earth-metals and chromium.

	Aluminum,	*Cerium.*	*Chromium.*
Ammonium sulphide .	White precipitate.	White precipitate.	Green precipitate.
Potassium hydroxide .	White precipitate. Soluble in KOH. Not re-precipitated by boiling.	White precipitate. Insoluble in KOH	Green precipitate. Soluble in KOH. Re-precipitated by boiling.
Ammonia water . . .	White precipitate.	White precipitate.	Green precipitate.
Ammonium carbonate	White precipitate.	White precipitate.	Green precipitate.

25. IRON. (*Ferrum.*)

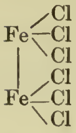
$Fe^{ii} = 55.9$ (55.88).

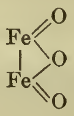
General remarks regarding the metals of the iron group. The six metals (Fe, Co, Ni, Mn, Cr, Zn) belonging to this group are distinguished by forming sulphides (chromium excepted) which are insoluble in water, but soluble in dilute mineral acids; they are, consequently, not precipitated from their neutral or acid solutions by hydrosulphuric acid, but by ammonium sulphide as sulphides (chromium as hydroxide); their oxides, hydroxides, carbonates, phosphates, and sulphides are insoluble; their chlorides, iodides, bromides, sulphates, and nitrates are soluble in water.

With the exception of zinc, these metals are magnetic; they decompose water at a red heat, the oxide being formed and hydrogen liberated; in dilute hydrochloric or sulphuric acid they dissolve with formation of chlorides or sulphates, respectively, and liberation of hydrogen.

With the exception of zinc, which is bivalent, the metals of the iron group are bivalent in some compounds, trivalent in others, and form a number of oxides, the higher of which show, in some cases, decidedly acid properties, as, for instance, chromic or manganic oxides.

The trivalence of the elements mentioned is now assumed to be due to the combining of two quadrivalent atoms of these elements. It is for this reason that we find in ferric, manganic, or chromic compounds always a double atom of these elements exerting a valence of six. The constitution of ferric chloride, Fe_2Cl_6, and ferric oxide, Fe_2O_3, may be graphically represented thus :





Occurrence in nature. Among all the heavy metals, iron is both the most useful and the most widely and abundantly diffused in nature. It is found, though usually in but small quantities, in nearly all forms of rock, clay, sand, and earth; its presence in these being indicated generally by their color (red, reddish-brown, or yellowish-red), as iron is the most common of all natural, inorganic coloring agents. It is found also, though in small quantities, in plants, and in somewhat larger proportions in the animal system, chiefly in the blood. In the metallic state iron is scarcely ever found, except in the meteorites or metallic masses which fall occasionally upon our earth out of space.

The chief compounds of iron found in nature are:

Hematite, ferric oxide,	Fe_2O_3.
Magnetic iron ore, ferrous-ferric oxide,	$FeO.Fe_2O_3$.
Spathic iron ore, ferrous carbonate,	$FeCO_3$.
Iron pyrites, bisulphide of iron,	FeS_2.

The carbonate and sulphate are found sometimes in spring waters, which, when containing considerable quantities of iron, are called chalybeate waters. Finally, iron is a constituent of some organic substances which are of importance in the animal system.

Manufacture of iron. There is no other metal manufactured in such immense quantities as iron, the use of which in thousands of different tools, machines, and appliances is highly characteristic of our present age. Iron is manufactured from the above-named oxides or the carbonate by heating them with coke and limestone in large blast furnaces, which have a somewhat cylindrical shape, and are constantly fed from above with a mixture of the substances named, while hot air is forced into the furnace through suitable apertures near its hearth. The chemical change which takes place in the upper and less heated part of the furnace is a deoxidation of the iron oxide by the carbon:

$$Fe_2O_3 + 3C = 3CO + 2Fe$$

The heat necessary for this decomposition and fusion of the reduced iron is produced by the combustion of the fuel, maintained by the oxygen of the air blown into the furnace. At the same time the lime and other bases combine with the silica contained in the ore, forming a fusible glass, called *cinder* or *slag.* The iron and slag collect at the bottom of the furnace, where they separate by gravity, and are run off every few hours.

Iron thus obtained is known as *cast-iron,* or *pig-iron,* and is not pure, but always contains, besides silicon (also sulphur, phosphorus, and various metals), a quantity of carbon varying from 2 to 5 per cent. It is the quantity of this carbon and its condition which imparts to the different kinds of iron different properties. *Steel* contains from 0.16 to 2 per cent., *wrought-* or *bar-iron* but very small quantities, of carbon. Wrought-iron is made from cast-iron by the process known as puddling, which is a burning-out of the carbon by oxidation, accomplished by agitating the molten mass in the presence of an oxidizing flame. Steel is made either from cast-iron by partially removing the carbon, or from wrought-iron by recombining it with carbon—*i. e.,* by agitating together molten wrought- and cast-iron in proper proportions.

Properties. The high position which iron occupies among the useful metals is due to a combination of valuable properties not found in any other metal. Although possessing nearly twice as great a tenacity or strength as any of the other metals commonly used in the metallic state, it is yet one of the lightest, its specific gravity being about 7.7. Though being when cold the least yielding or malleable of the metals in common use, its ductility when heated is such that it admits of being rolled into the thinnest sheets and drawn into the finest wire, the strength of which is so great that a wire of one-tenth of an inch in diameter is capable of sustaining 700 pounds. Finally, iron is, with the exception of platinum, the least fusible of all the useful metals.

Iron is little affected by dry air, but is readily acted upon by moist air, when ferric oxide and ferric hydroxide (rust) are formed.

Iron forms two series of compounds, distinguished as ferrous and ferric compounds; in the former, iron is bivalent, in the latter, apparently trivalent, because, as shown above, the double atom exerts a valence of six. Almost all ferrous compounds show a tendency to pass into ferric compounds when exposed to the air, or more readily when treated with oxidizing agents, such as nitric acid, chlorine, etc. As the reaction of iron in ferrous and ferric compounds differs considerably, they must be studied separately.

Reduced iron, Ferrum reductum. This is metallic iron, obtained as a very fine, grayish-black, lustreless powder by passing hydrogen gas (purified and dried by passing it through sulphuric acid) over ferric oxide, heated in a glass tube:

$$Fe_2O_3 + 6H = 3H_2O + 2Fe.$$

The official article should have at least 80 per cent. of metallic iron.

Ferrous oxide, FeO (*Monoxide or suboxide of iron*). This compound is little known in the separate state, as it has (like most ferrous compounds) a great tendency to absorb oxygen from the air. The *ferrous hydroxide*, $Fe(OH)_2$, may be obtained by the addition of any alkaline hydroxide to the solution of any ferrous salt, when a white precipitate is produced which rapidly turns bluish-green, dark-gray, black, and finally brown, in consequence of absorption of oxygen (see Plate I., 2):

$$FeSO_4 + 2NH_4OH = (NH_4)_2SO_4 + Fe(OH)_2;$$
$$2Fe(OH)_2 + O + H_2O = Fe_2(OH)_6.$$

The precipitation of ferrous hydroxide is not complete, some iron always remaining in solution.

Ferrous oxide is a strong base, uniting with acids to form salts, which have usually a pale-green color.

Ferric oxide, Fe_2O_3. A reddish-brown powder, which may be obtained by heating ferric hydroxide to expel water:

$$Fe_2(OH)_6 = Fe_2O_3 + 3H_2O.$$

It is a feeble base; its salts show usually a brown color.

Ferric hydroxide, Ferric hydrate, Ferri oxidum hydratum, $Fe_2(OH)_6$ =213.8 (*Hydrated oxide of iron, Per- or sesqui-oxide, Red oxide of iron*), is obtained by precipitation of ferric sulphate or ferric chloride by ammonium or sodium hydroxide (see Plate I., 3):

$$Fe_2(SO_4)_3 + 6NH_4OH = 3[(NH_4)_2SO_4] + Fe_2(OH)_6.$$

Precipitation is complete, no iron remaining in solution as in the case of ferrous salts.

Ferric hydroxide is a reddish-brown powder, sometimes used as an antidote in arsenic poisoning; for this purpose it is not used in the dry state, but after having been freshly precipitated and washed, it is mixed with water, and this mixture used. Recently precipitated and consequently highly divided ferric hydroxide combines more readily with arsenous acid than the hydroxide which has been kept some time, or which has been dried, and thereby assumed a denser condition.

Hydrated oxide of iron with magnesia, U. S. P., is a mixture made by adding magnesia to a solution of ferric sulphate, when magnesium sulphate and ferric hydroxide are formed; the two substances are not separated from each other, the mixture being intended for immediate administration as an antidote in cases of arsenic poisoning.

Ferrous-ferric oxide, $FeO.Fe_2O_3$ (*Magnetic oxide*). This compound, which shows strong magnetic properties, has been mentioned above as one of the iron ores, and is known as *loadstone*. It has a metallic lustre and iron-black color, and is produced artificially by the combustion of iron in oxygen, or in the hydrated state by the addition of ammonium hydroxide to a mixture of solutions of ferrous and ferric salts.

Iron trioxide, FeO_3. Not known in a separate state, but in combination with alkalies. In these compounds, called *ferrates*, FeO_3 acts as an acid oxide, analogous to chromium trioxide, CrO_3, in chromates. The composition of potassium ferrate is K_2FeO_4.

Ferrous Chloride, $FeCl_2$ (*Protochloride of iron*), is obtained as a pale-green solution by dissolving iron in hydrochloric acid:

$$Fe + 2HCl = FeCl_2 + 2H.$$

By evaporation of the solution, the dry salt may be obtained. The solution and salt absorb oxygen very readily:

$$3FeCl_2 + O = FeO + Fe_2Cl_6.$$

Ferric chloride, ferrous, and afterward ferric oxide, are formed.

Ferric chloride, Ferri chloridum, $Fe_2Cl_6.12H_2O = 540.2$ (*Chloride, sesqui-chloride, or perchloride of iron*), is obtained by adding to the solution of ferrous chloride (obtained as mentioned above) hydrochloric and nitric acids in sufficient quantities, and applying heat until complete oxidation has taken place. The nitric acid oxidizes the hydrogen of the hydrochloric acid to water, while the chlorine combines with the ferrous chloride, nitrogen dioxide being formed also:

$$6FeCl_2 + 2HNO_3 + 6HCl = 3Fe_2Cl_6 + 4H_2O + 2NO.$$

By sufficient evaporation of the solution, ferric chloride is obtained as a crystalline mass of an orange-yellow color; it is very deliquescent, has an acid reaction, and a strongly styptic taste. The water of crystallization cannot be expelled by heat, because heat decomposes the salt, free hydrochloric acid and ferric oxide being formed.

Experiment 26. Dissolve by the aid of heat 1 gramme of fine iron wire in about 4 c.c. of hydrochloric acid, previously diluted with 2 c.c. of water.

Filter the warm solution of ferrous chloride, mix it with 2 c.c. of hydrochloric acid, and add to it slowly and gradually about 0.6 c.c. of nitric acid. Evaporate in a fume chamber as long as red vapors escape; then test a few drops with potassium ferricyanide, which should not give a blue precipitate; if it does, the solution has to be heated with a little more nitric acid until the conversion into ferric chloride is complete and the potassium ferricyanide produces no precipitate. Ferric chloride thus obtained may be mixed with 4 c.c. of hot water and set aside, when it forms a solid mass of $Fe_2Cl_6.12H_2O$. How much $FeCl_2$, how much Fe_2Cl_6, and how much $Fe_2Cl_6.12H_2O$ can be obtained from 1 gramme of iron?

Solution of chloride of iron, Liquor ferri chloridi, U. S. P. This is a solution in water, containing 37.8 per cent. of the anhydrous ferric chloride and some free hydrochloric acid. It is a reddish-brown liquid of specific gravity 1.405, having the taste and reaction of the dry salt. This solution, mixed with 3 volumes of alcohol and left standing in a closed vessel for at least three months, forms the *tincture of chloride of iron*, *Tinctura ferri chloridi*, U. S. P. By the action of the alcohol on ferric chloride this is reduced to the ferrous state, while at the same time a number of other compounds are formed, imparting to the liquid an ethereal odor.

Dialyzed iron is an aqueous solution of about 5 per cent. of ferric hydroxide with some ferric chloride. It is made by slowly adding to a solution of ferric chloride, ammonium hydroxide as long as the precipitate of ferric hydroxide formed is redissolved in the ferric chloride solution, on shaking violently. The clear solution thus obtained is placed in a dialyzer floating in water, which latter is renewed every day until it shows no reaction with silver nitrate. The ammonium chloride passes through the membrane of the dialyzer into the water, while all iron as hydroxide with some chloride is left in solution.

The combination of an oxide or hydroxide with a normal salt is called usually a basic salt or oxy-salt; dialyzed iron is a highly basic oxychloride of iron.

Ferrous iodide, FeI_2. When water is poured upon a mixture of metallic iron (fine wire is best) and iodine, the two elements combine directly, forming a pale-green solution of ferrous iodide, from which the salt may be obtained by evaporation. As it is oxidized and decomposed easily by the action of the air, an official preparation, the *saccharated ferrous iodide*, U. S. P., is made by adding about 80 parts of sugar of milk to 20 parts of ferrous iodide; the sugar prevents, to some extent, rapid oxidation.

Experiment 27. Cover some fine iron wire with water, heat gently, and add iodine in fragments as long as the red color of iodine disappears. Notice that the iron is dissolved gradually, the result of the reaction being the formation of a pale-green solution of ferrous iodide.

Ferrous bromide, $FeBr_2$. Made analogously to ferrous iodide, by the action of bromine on metallic iron.

Ferrous sulphide, FeS. Easily obtained as a black, brittle mass, by heating iron filings with sulphur, when the elements combine. It is used chiefly for liberating hydrogen sulphide, by the addition of sulphuric acid. Iron combines with sulphur in several proportions; some of these iron sulphides are found in nature.

Ferrous sulphate, Ferri sulphas, $FeSO_4.7H_2O = 277.9$ (*Sulphate of iron, Green vitriol, Copperas*). Obtained by dissolving iron in dilute sulphuric acid, evaporating, and crystallizing:

$$Fe + H_2SO_4 = 2H + FeSO_4.$$

Also obtained as a by-product in some branches of chemical industry, and by heap-roasting of the native iron sulphide:

$$FeS_2 + 6O = FeSO_4 + SO_2.$$

Ferrous sulphate crystallizes in large, bluish-green prisms; it is soluble in water, insoluble in alcohol. Exposed to the air, it loses water of crystallization, and absorbs oxygen.

The *dried ferrous sulphate*, U. S. P., is made by expelling about 4 molecules of water by heating to 100° C. (212° F.); the *granulated* (*precipitated*) *ferrous sulphate* is made by pouring a strong aqueous solution of ferrous sulphate, slightly acidulated with sulphuric acid, into alcohol, when ferrous sulphate separates as a crystalline powder, which is washed and dried.

Ferric sulphate, $Fe_2(SO_4)_3$. The solution of this salt, *Liquor ferri tersulphatis*, *Solution of ferric sulphate*, U. S. P., is made by adding sulphuric and nitric acids to a solution of ferrous sulphate and heating:

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3[Fe_2(SO_4)_3] + 2NO + 4H_2O.$$

The action of nitric acid is similar to that described above under ferric chloride. The hydrogen of the sulphuric acid is oxidized, and the radical SO_4 unites with the ferrous sulphate, nitrogen dioxide being liberated.

Solution of ferric sulphate is used in the preparation of *Ferric* *ammonium sulphate, Ferri et ammonii sulphas,* $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$ (*iron alum* or *ammonio-ferric alum*), which is made by mixing solution of ferric sulphate with ammonium sulphate and crystallizing. The salt has a pale violet color and is readily soluble in water.

Solution of ferric subsulphate, Liquor ferri subsulphatis (*Monsel's solution*). This is a solution similar to the preceding, but contains less sulphuric acid, and is, therefore, looked upon as a basic ferric sulphate, of the doubtful composition $5[Fe_2(SO_4)_3].Fe_2(OH)_6$.

Ferric nitrate, $Fe_2(NO_3)_6$. A 6 per cent. solution of this salt is official, under the name *Solution of ferric nitrate, Liquor ferri nitratis,* U. S. P., and is made by dissolving ferric hydroxide in nitric acid:

$$Fe_2(OH)_6 + 6HNO_3 = 6H_2O + Fe_2(NO_3)_6.$$

It is an amber-colored, or reddish, acid liquid.

Ferrous carbonate, $FeCO_3$. Occurs in nature; may be obtained by mixing solutions of ferrous sulphate and sodium carbonate or bicarbonate:

$$FeSO_4 + 2NaHCO_3 = Na_2SO_4 + FeCO_3 + CO_2 + H_2O.$$

The precipitate is first nearly white, but soon assumes a gray color from oxidation. The *saccharated carbonate of iron,* U. S. P., is made by mixing the washed precipitate with sugar, and drying. The sugar prevents, to some extent, rapid oxidation. The preparation contains 15 per cent. of ferrous carbonate.

Ferric carbonate does not exist, the affinity between the feeble ferric oxide and the weak carbonic acid not being sufficient to unite them chemically.

Ferrous phosphate, $Fe_3(PO_4)_2$. When sodium phosphate is added to solution of ferrous sulphate, a precipitate of the composition $FeHPO_4$ is formed:

$$Na_2HPO_4 + FeSO_4 = FeHPO_4 + Na_2SO_4.$$

If, however, sodium acetate is added, a precipitate of the composition $Fe_3(PO_4)_2$ is formed:

$$3FeSO_4 + 2Na_2HPO_4 = Fe_3(PO_4)_2 + 2Na_2SO_4 + H_2SO_4.$$

The sulphuric acid liberated, as shown in this formula, decomposes the sodium acetate, forming sodium sulphate and free acetic acid. Ferrous phosphate is a slate-colored powder, absorbing oxygen readily, becoming darker in color.

Analytical reactions.

	Ferrous salts. (Use $FeSO_4$.)	*Ferric salts.* (Use Fe_2Cl_6.)
1. Ammonium sulphide.	Black precipitate of ferrous sulphide (Plate I., 1). $FeSO_4 + (NH_4)_2S = (NH_4)_2SO_4 + FeS.$	Black precipitate of ferrous sulphide mixed with sulphur. $Fe_2Cl_6 + 3[(NH_4)_2S] = 6NH_4Cl + 2FeS + S.$
2. Hydrosulphuric acid.	No change.	Ferric salts are converted into ferrous salts with precipitation of sulphur. $Fe_2Cl_6 + H_2S = 2FeCl_2 + 2HCl + S.$
3. Ammonium, sodium, or potassium hydroxide.	White precipitate of ferrous hydroxide soon turning green, black, and brown. Precipitation not complete (Plate I., 2). $FeCl_2 + 2NaOH = 2NaCl + Fe(OH)_2.$	Reddish-brown precipitate of ferric hydroxide Precipitation is complete (Plate I, 3). $Fe_2Cl_6 + 6(NH_4OH) = 6NH_4Cl + Fe_2(OH)_6.$
4. Ammonium, sodium, or potassium carbonate.	White precipitate of ferrous carbonate, soon turning darker. $FeCl_2 + Na_2CO_3 = 2NaCl + FeCO_3.$	Reddish-brown precipitate of ferric hydroxide, with liberation of carbon dioxide (Plate I., 3). $Fe_2Cl_6 + 3Na_2CO_3 + 3H_2O = 6NaCl + Fe_2(OH)_6 + 3CO_2.$
5. Alkali phosphates or arsenates.	Almost white precipitate, soon turning darker.	A yellowish-white precipitate is produced.
6. Potassium ferrocyanide. $K_4Fe(CN)_6$.	Almost white precipitate, soon turning blue by absorption of oxygen (Plate I., 4).	Dark-blue precipitate of ferric ferrocyanide, or Prussian blue. Decomposed by alkalies; insoluble in acids (Plate I., 5). $2Fe_2Cl_6 + 3[K_4Fe(CN)_6] = 12KCl + Fe_4 3[Fe(CN)_6].$
7. Potassium ferricyanide. $K_6Fe_2(CN)_{12}$.	Blue precipitate of ferrous ferricyanide, or Turnbull's blue. $3FeCl_2 + K_6Fe_2(CN)_{12} = 6KCl + Fe_3Fe_2(CN)_{12}.$	No precipitate is produced, but the liquid is darkened to a greenish-brown hue.
8. Tannic acid.	No change, provided oxidation of the ferrous salt has not taken place.	A dark greenish-black precipitate of ferric tannate is produced (Plate VII., 3).
9. Potassium sulphocyanate. KCNS.	As above.	Deep blood-red precipitate of ferric sulphocyanate (Plate I., 6.)

Ferric phosphate, $Fe_2(PO_4)_2$, may be obtained from ferric chloride solution by precipitation with an alkali phosphate. The soluble ferric phosphate of the U. S. P. is a scale compound. (See index.)

Ferric hypophosphite, Ferri hypophosphis, $Fe_2(H_2PO_2)_6 = 501.8$ (*Hypophosphite of iron*). Made by dissolving ferric hydroxide in hypophosphorous acid, and evaporating. It is a grayish-white powder, slightly soluble in water, soluble in hydrochloric acid, in hypophosphorous acid, and in a warm, concentrated solution of an alkali citrate.

26. MANGANESE—CHROMIUM—COBALT—NICKEL.

Manganese, Mn = 54.8. Manganese is found either as dioxide (Black oxide of manganese, pyrolusite), MnO_2, or as sesquioxide, Mn_2O_3. In small quantities it is a constituent of many minerals.

Metallic manganese resembles iron in its physical and chemical properties, and may be obtained by reducing the carbonate with charcoal. Manganese is darker in color than iron, considerably harder, and somewhat more easily oxidized.

Oxides of manganese. Four well-defined compounds of manganese with oxygen are known in the separate state, and two others only in combination with other elements. These oxides are :

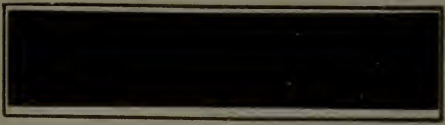
Manganous oxide (monoxide or protoxide),		MnO.
Manganous manganic oxide,		$MnO\ Mn_2O_3 = Mn_3O_4$.
Manganic oxide (sesquioxide),		Mn_2O_3.
Manganese dioxide (binoxide, peroxide, black oxide),		MnO_2.
Manganic acid,	Not known in a separate state,	$H_2O + MnO_3$.
Permanganic acid,		$H_2O + Mn_2O_7$.

QUESTIONS.—241. Which metals belong to the "iron group," and what are their general properties? 242. How is iron found in nature, and what compounds are used in its manufacture? 243. Describe the process for manufacturing iron on a large scale, and state the difference between cast-iron, wrought-iron, steel, and reduced iron. 244. State the composition and mode of preparation of ferrous and ferric hydroxides. What are their properties? 245. Describe in words and chemical symbols the process for making ferric chloride. What is tincture of chloride of iron? 246. How are ferrous iodide and bromide made? 247. State the properties of ferrous sulphate. Under what other names is it known, and how is it made? 248. What change takes place when soluble carbonates are added to soluble ferrous and ferric salts? 249. Mention agents by which ferrous compounds may be converted into ferric compounds, and these into ferrous compounds. Explain the chemical changes taking place. 250. Mention tests for ferrous and ferric compounds.

PLATE I.

IRON. COBALT. NICKEL.

1



Ferrous sulphide, precipitated from ferrous solutions by ammonium sulphide.

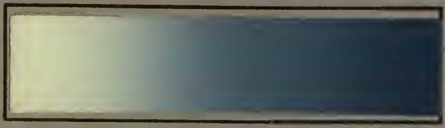
2

Ferrous hydroxide passing into ferric hydroxide. Ferrous solutions precipitated by alkali hydroxides.

3

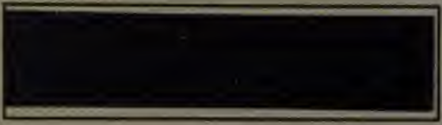
Ferric hydroxide, precipitated from ferric solutions by alkali hydroxides.

4



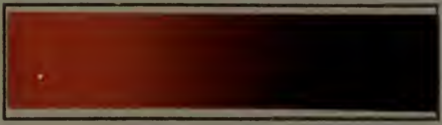
Ferrous solutions, precipitated by potassium ferrocyanide.

5



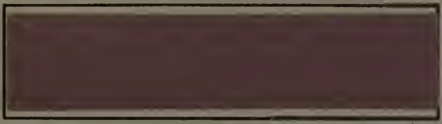
Ferric solutions, precipitated by potassium ferrocyanide, or, Ferrous solutions precipitated by potassium ferricyanide.

6



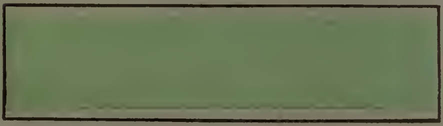
Ferric solutions, treated with alkali sulphocyanates.

7



Cobaltous carbonate, precipitated from cobaltous solutions by sodium carbonate.

8



Nickelous carbonate, precipitated from nickelous solutions by sodium carbonate.

Manganous oxide is a greenish-gray powder, obtainable by heating the carbonate; or as a nearly white hydroxide by precipating a manganous salt by sodium hydroxide. It is a strong base, saturating acids completely, and forming salts which have generally a rose color or a pale reddish tint.

Manganese dioxide, Mangani oxidum nigrum, $MnO_2 = 86.8$. This is by far the most important compound of manganese, as it is largely used for generating chlorine:

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + 2Cl.$$

It is a heavy, grayish-black, crystalline mineral, liberating oxygen when heated to redness:

$$3MnO_2 = Mn_3O_4 + 2O.$$

The official article should contain at least 66 per cent. of MnO_2.

Manganous sulphate, Mangani sulphas, $MnSO_4.4H_2O = 222.8$, may be obtained by dissolving the oxide or dioxide in sulphuric acid; in the latter case oxygen is evolved:

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$

As manganese dioxide generally contains iron oxide, the solution contains sulphates of both metals. By evaporating to dryness and strongly igniting, the iron salt is decomposed. The ignited mass is now lixivated with water, and the filtered solution evaporated for crystallization.

It is an almost colorless, or pale rose-colored substance, isomorphous with the sulphates of magnesium and zinc; it is easily soluble in water.

KMNO4

Potassium permanganate, Potassii permanganas, $KMnO_4 =$ 157.8. Whenever a compound (any oxide or salt) of manganese is fused with alkali carbonates (or hydroxides) and alkali nitrates (or chlorates) the manganese is converted into manganic acid, which combines with the alkali, forming potassium (or sodium) manganate:

$$3MnO_2 + 3K_2CO_3 + KClO_3 = 3K_2MnO_4 + 3CO_2 + KCl.$$

The fused mass has a dark-green color, and when dissolved in water gives a dark emerald-green solution, from which, by evaporation, green crystals of *potassium manganate* may be obtained.

The green solution is decomposed easily by any acid (or even by water in large quantity) into a red solution of potassium permanganate and a precipitate of manganese dioxide.

$$3K_2MnO_4 + 2H_2SO_4 = MnO_2 + 2K_2SO_4 + 2KMnO_4 + 2H_2O.$$

By evaporation and crystallization potassium permanganate is obtained in slender, prismatic crystals, of a dark-purple color, and a somewhat metallic lustre. The solution in water has a deep purple, or, when highly diluted, a pink color (Plate II., 1). It is a powerful oxidizing agent, and an excellent disinfectant, both properties being due to the facility with which a portion of the oxygen is given off to any substance which has affinity for it. If the oxidation takes place in the absence of an acid, a lower oxide of manganese is formed, which separates as an insoluble substance. If an acid is present, both the potassium and manganese combine with it, forming salts, thus:

$$2(KMnO_4) + 6HCl + x = 2KCl + 2MnCl_2 + 3H_2O + xO_5.$$

x represents here any substance capable of combining with oxygen while in solution.

Experiment 28. Heat in a porcelain crucible a mixture of 2 grammes manganese dioxide, 2 grammes potassium hydroxide, and 1 gramme potassium chlorate, until the fused mass has turned dark-green. Dissolve the cooled mass with water, filter the green solution of potassium manganate, and pass carbon dioxide through it until it has assumed a purple color, showing that the conversion into permanganate is complete. Notice that the acidified solution is readily decolorized by ferrous salts and other deoxidizing agents.

Analytical reactions.

(Manganous sulphate, $MnSO_4$, may be used.)

1. Ammonium sulphide produces a yellowish-pink or flesh-colored precipitate of hydrated manganous sulphide, $MnS.H_2O$, soluble in acetic and in mineral acids (Plate II., 2):

$$MnSO_4 + (NH_4)_2S = (NH_4)_2SO_4 + MnS.$$

2. Ammonium (or sodium) hydroxide produces a white precipitate of manganous hydroxide, which soon darkens by absorption of oxygen (Plate II., 3) and dissolves in oxalic acid with a rose-red color:

$$MnCl_2 + 2NH_4OH = 2NH_4Cl + Mn(OH)_2.$$

3. Sodium (or potassium) carbonate produces a nearly white precipitate of manganous carbonate:

$$MnSO_4 + Na_2CO_3 = Na_2SO_4 + MnCO_3.$$

4. Any compound of manganese heated on platinum foil with a mixture of sodium carbonate and nitrate forms a bluish-green mass, giving a green solution in water, which turns red on addition of an acid. (See explanation above.)

5. Manganese compounds fused with borax on a platinum wire give a violet color to the borax bead.

6. Traces of manganese may be detected by boiling with dilute nitric acid and red lead, when the solution acquires a reddish-purple color due to the formation of permanganic acid.

Chromium, Cr = 52. Found in nature almost exclusively as chromite, or chrome-iron ore, $FeO.Cr_2O_3$, a mineral analogous in composition to magnetic iron ore, $FeO.Fe_2O_3$. The name chromium, from the Greek χρῶμα (chroma), color, was given to this metal on account of the beautiful colors of its different compounds, none of which is colorless. Chromium forms two basic oxides, CrO and Cr_2O_3, and an acid oxide, CrO_3, the combinations and reactions of which have to be studied separately. While chromium is closely allied to aluminum and iron on one side, it also shows a resemblance to sulphur, as indicated by the trioxide, CrO_3, and the acid, H_2CrO_4, which are analogous to SO_3 and H_2SO_4. Moreover, the barium and lead salts of chromic and sulphuric acids are both insoluble.

Potassium dichromate, Potassii bichromas, $K_2Cr_2O_7 = 294$ (*Bichromate or red chromate of potassium*). This salt is by far the most important of all chromium compounds, and is the source from which they are obtained.

Potassium dichromate is manufactured on a large scale by exposing a mixture of the finely ground chrome-iron ore with potassium carbonate and calcium hydroxide to the heat of an oxidizing flame in a reverberatory furnace, when both constituents of the ore become oxidized, ferric oxide and chromic acid being formed, the latter combining with the potassium, forming normal potassium chromate, K_2CrO_4.

$$2(FeOCr_2O_3) + 4K_2CO_3 + 7O = Fe_2O_3 + 4CO_2 + 4(K_2CrO_4).$$

By treating the furnaced mass with water a yellow solution of potassium chromate is obtained, which, upon the addition of sulphuric acid, is decomposed into potassium dichromate and potassium sulphate:

$$2(K_2CrO_4) + H_2SO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O.$$

The two salts may be separated by crystallization. Potassium dichromate forms large, orange-red, transparent crystals, which are easily soluble in water; heated by itself oxygen is evolved, heated with hydrochloric acid chlorine is liberated, heated with organic matter or reducing agents these are oxidized.

To explain the constitution of dichromates we have to assume that chromic anhydride, CrO_3, is capable of forming two acids:

$$CrO_3 + H_2O = H_2CrO_4 = \text{Chromic acid.}$$
$$2CrO_3 + H_2O = H_2Cr_2O_7 = \text{Dichromic acid.}$$

Chromium trioxide, Acidum Chromicum, $CrO_3 = 100$ (*Chromic acid, Chromic anhydride*), is prepared by adding sulphuric acid to a saturated solution of potassium dichromate, when chromium trioxide separates in crystals:

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + H_2O + 2CrO_3.$$

Thus prepared, its forms deep purplish-red, needle-shaped crystals, which are deliquescent, and very soluble in water; it is powerfully corrosive, and one of the strongest oxidizing agents; the solution in water has strong acid properties; it combines with metallic oxides, forming chromates and dichromates.

Experiment 29. Dissolve a few grammes of potassium dichromate in water and add to 4 volumes of the cold saturated solution 5 volumes of strong sulphuric acid; chromium trioxide separates on cooling. Collect the crystals on asbestos, wash them with a little nitric acid, and dry them by passing warm dry air through a tube in which they have been placed for this purpose.

Chromic oxide, Cr_2O_3 (*Sesquioxide of chromium*), is obtained by heating potassium dichromate with sulphur, when potassium sulphate and chromic oxide are formed:

$$K_2Cr_2O_7 + S = K_2SO_4 + Cr_2O_3.$$

By washing the heated mass with water, the chromic oxide is left as a green powder, which is insoluble in water and in acids; it is a basic oxide combining with acids to form salts; it is used as a green color, especially in the manufacture of painted glass and porcelain.

Chromic hydroxide, $Cr_2(OH)_6$. A solution of potassium dichromate may be deoxidized by the action of hydrosulphuric acid, sulphurous acid, alcohol, or any other deoxidizing agent, in the presence of sulphuric or hydrochloric acid:

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S = K_2SO_4 + 7H_2O + 3S + Cr_2(SO_4)_3.$$

As shown by this formula, the sulphates of potassium and chromium are formed and remain in solution, while sulphur is precipitated, the hydrogen of the hydrosulphuric acid having been oxidized and converted into water.

By adding ammonium hydroxide to the solution thus obtained, chromic hydroxide is precipitated as a bluish-green gelatinous substance:

$$Cr_2(SO_4)_3 + 6NH_4OH = 3[(NH_4)_2SO_4] + Cr_2(OH)_6.$$

By dissolving this hydroxide in the different acids, the various salts, such as chloride, Cr_2Cl_6, sulphate, etc., are obtained. Chromic sulphate, similar to aluminum sulphate, combines with potassium or ammonium sulphate and water, forming *chrome alum*, $K_2SO_4.Cr_2(SO_4)_3 24H_2O$; it is a purple salt, and is isomorphous with other alums.

Analytical reactions.

a. Of chromic acid or chromates.

(Use potassium chromate, K_2CrO_4.)

1. Hydrogen sulphide added to an acidified solution of a chromate changes the red color into green with precipitation of sulphur. The solution now contains chromium in the basic form. (See explanation above.) (Plate II., 4.) The conversion of chromic acid into oxide is more readily accomplished by heating the chromic solution with alcohol and hydrochloric acid; the alcohol is partly oxidized, being converted into aldehyde.

2. Soluble lead salts produce a yellow precipitate of lead chromate (chrome yellow), $PbCrO_4$, insoluble in acetic, soluble in hydrochloric acid and in sodium hydroxide (Plate II., 6):

$$K_2CrO_4 + Pb(NO_3)_2 = PbCrO_4 + 2KNO_3.$$

3. Barium chloride produces a pale yellow precipitate of barium chromate, $BaCrO_4$:

$$K_2CrO_4 + BaCl_2 = BaCrO_4 + 2KCl.$$

4. Silver nitrate produces a dark-red precipitate of silver chromate, Ag_2CrO_4 (Plate II., 8):

$$2AgNO_3 + K_2CrO_4 = 2KNO_3 + Ag_2CrO_4.$$

5. Mercurous nitrate produces a red precipitate of mercurous chromate, Hg_2CrO_4.

b. Of salts of chromium.

(Use chrome-alum or chromic chloride, Cr_2Cl_6.)

6. To chromic chloride or sulphate add ammonium hydroxide or ammonium sulphide: in both cases the green hydroxide of chromium, $Cr_2(OH)_6$, is precipitated (Plate II., 5):

$$Cr_2Cl_6 + 3[(NH_4)_2S] + 6H_2O = 6NH_4Cl + 3H_2S + Cr_2(OH)_6.$$

7. Potassium or sodium hydroxide causes a similar green precipitate of chromic hydroxide, which is soluble in an excess of the reagent, but is re-precipitated on boiling for a few minutes.

c. Of chromium in any form.

8. Compounds of chromium, when mixed with sodium (or potassium) carbonate and nitrate, give, when heated upon platinum foil, a yellow mass of the alkali chromate.

9. Compounds of chromium impart a green color to the borax bead.

Cobalt and Nickel, Co = 58.7, Ni = 58.6. These two metals show much resemblance to each other in their chemical and physical properties, and occur in nature often associated with each other as sulphides or arsenides.

Both metals are nearly silver-white; the salts of cobalt show generally a red, those of nickel a green color. The solutions of both metals give a black precipitate of the respective sulphides on the addition of ammonium sulphide. Ammonium hydroxide produces in solutions of cobalt a blue, in solutions of nickel a green precipitate of the hydroxides, both of which are soluble in an excess of the reagent; potassium or sodium hydroxide produces similar precipitates, which are insoluble in an excess.

Cobalt is used chiefly when in a state of combination (for coloring glass blue); nickel when in the metallic state. (German silver is an alloy of nickel, copper, and zinc.)

27. ZINC.

$Zn^{ii} = 65.1$.

Occurrence in nature. Zinc is found chiefly either as sulphide (zinc-blende), ZnS, or as carbonate (calamine), $ZnCO_3$; also it occurs in combination with silicic acid as silicate and with oxygen as the red oxide.

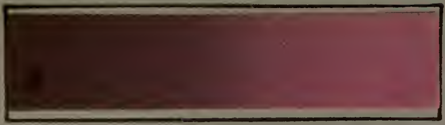
Metallic Zinc is obtained by heating in retorts the oxide or carbonate mixed with charcoal, when decomposition takes place.

Questions.—251. How is manganese found in nature? 252. Mention the different oxides of manganese. What is the binoxide used for? 253. What is the color of manganese salts, of manganates, and of permanganates? 254. How is potassium permanganate made; what are its properties, and what is it used for? 255. Give tests for manganese. 256. State composition and properties of potassium dichromate. 257. How is chromium trioxide made; what are its properties; what is it used for; and under what other name is it known? 258. By what process may chromium sesquioxide be converted into chromates? 259. What is the composition of the oxide and hydroxide of chromium, and how are they made? 260. Mention tests for chromates and chromium salts.

PLATE II.

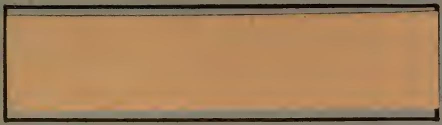
MANGANESE. CHROMIUM.

1



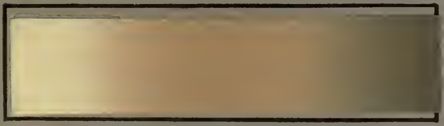
Potassium permanganate solution, more or less saturated. Borax-bead colored by manganese.

2



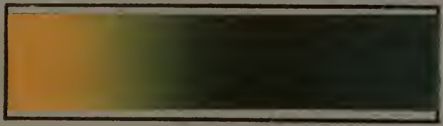
Manganous sulphide, precipitated from manganous solutions by ammonium sulphide.

3



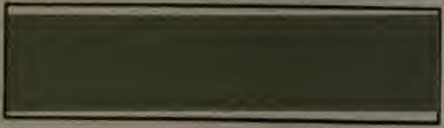
Manganous hydroxide passing into the higher oxides. Manganous solutions precipitated by alkali hydroxides.

4



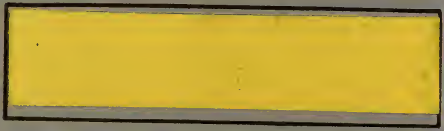
Potassium dichromate solution deoxidized by reducing agents.

5



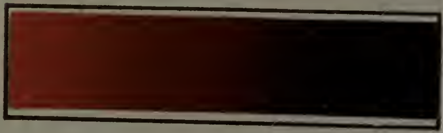
Chromic hydroxide, precipitated from chromic solutions by alkali hydroxides.

6



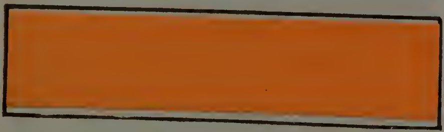
Lead chromate. precipitated from soluble chromates by lead acetate.

7



Silver chromate, precipitated from neutral chromates by silver nitrate.

8



Mercurous chromate, precipitated from neutral chromates by mercurous solutions.

The liberated metal is vaporized, and distils into suitable receivers, where it solidifies.

Zinc is a bluish-white metal, which slowly tarnishes in the air, becoming coated with a film of oxide and carbonate; it has a crystalline structure and is, under ordinary circumstances, brittle; when heated to about 130°–150° C. (260°–302° F.) it is malleable, and may be rolled or hammered without fracture. Zinc thus treated retains this malleability when cold; the sheet-zinc of commerce is thus made. When zinc is further heated to about 200° C. (392° F.), it loses its malleability and becomes so brittle that it may be powdered; at 410° C. (760° F.) it fuses, and at a bright-red heat it boils, volatilizes, and, if air be not excluded, burns with a splendid greenish-white light, generating the oxide.

Zinc is used by itself in the metallic state or fused together with other metals (German silver and brass contain it); galvanized iron is iron coated with metallic zinc.

Zinc is a bivalent metal, forming but one oxide and one series of salts, all of which have a white color.

Zinc oxide, Zinci oxidum, $ZnO = 81.1$ (*Flores zinci, Zinc-white*), may be obtained by burning the metal, but if made for medicinal purposes, by heating the carbonate, when carbon dioxide and water escape and the oxide is left:

$$3[Zn(OH)_2].2ZnCO_3 = 5ZnO + 2CO_2 + 3H_2O.$$

It is an amorphous, white, tasteless powder, insoluble in water, soluble in acids; when strongly heated it turns yellow, but on cooling resumes the white color.

Zinc hydroxide, $Zn(OH)_2$, is obtained by precipitating zinc salts with the hydroxide of sodium or ammonium; the precipitate, however, is soluble in an excess of either of the alkali hydroxides.

Zinc chloride, Zinci chloridum, $ZnCl_2 = 135.9$. Made by dissolving zinc or zinc carbonate in hydrochloric acid and evaporating the solution to dryness:

$$Zn + 2HCl = ZnCl_2 + 2H.$$

It is met with either as a white crystalline powder, or in white opaque pieces; it is very deliquescent and easily soluble in water and alcohol; it combines readily with albuminoid substances; it fuses at about 115° C. (239° F.), and is volatilized, with partial decomposition, at a higher temperature.

Zinc bromide, Zinci bromidum, $ZnBr_2 = 224.7$. Obtained analogously to the chloride by dissolving zinc in hydrobromic acid; it is a white powder, resembling the chloride in its properties.

Zinc iodide, Zinci iodidum, $ZnI_2 = 318.1$. The two elements zinc and iodine combine readily when heated with water; the colorless solution when evaporated to dryness yields a powder whose physical properties resemble those of the chloride.

Zinc carbonate, Zinci carbonas præcipitatus, $2(ZnCO_3).3[Zn(OH_2)] = 547.5$ (*Precipitated carbonate of zinc*). Solutions of equal quantities of zinc sulphate and sodium carbonate are mixed and boiled, when a white precipitate is formed, which is a mixture of the carbonate and hydroxide of zinc, corresponding more or less to the formula given above.

$$5ZnSO_4 + 5Na_2CO_3 + 3H_2O = 3CO_2 + 5Na_2SO_4 + 2(ZnCO_3).3[Zn(OH)_2].$$

Precipitated zinc carbonate is a white, impalpable powder, odorless and tasteless, insoluble in water, soluble in acids and in ammonia water.

Zinc sulphate, Zinci sulphas, $ZnSO_4.7H_2O = 287.1$ (*White vitriol*), is obtained by dissolving zinc in dilute sulphuric acid:

$$H_2SO_4 + xH_2O + Zn = ZnSO_4 + xH_2O + 2H.$$

If zinc be added to strong sulphuric acid, no decomposition takes place: no sufficient explanation has as yet been given for this fact.

Zinc sulphate forms small, colorless crystals, which are isomorphous with magnesium sulphate; it is easily soluble in water.

Experiment 30. Use the liquid obtained when performing Experiment 2, or, if not left, dissolve a few grammes of metallic zinc in dilute sulphuric acid, filter the solution, evaporate sufficiently, and set aside for crystallization. Use the zinc sulphate thus obtained for the analytical reactions. State the quantity of dilute sulphuric acid required for dissolving 5 grammes of zinc, and the quantity of crystallized zinc sulphate which may be obtained.

Zinc phosphide, Zinci phosphidum, $Zn_3P_2 = 257.3$. The two elements zinc and phosphorus combine readily when the latter is thrown upon melted zinc, forming a grayish-black powder, or minutely crystalline, friable fragments, having a metallic lustre on the fractured surface.

Antidotes. Soluble zinc salts (sulphate, chloride) have a poisonous effect. If the poison have not produced vomiting, this should be induced. Milk, white of egg, or, still better, some substance containing tannic acid (with which zinc forms an insoluble compound) should be given.

Analytical reactions.

(Zinc sulphate, $ZnSO_4$, may be used.)

1. Add to solution of a zinc salt ammonium sulphide; a white precipitate of zinc sulphide, ZnS, is produced. (Zinc sulphide is the only white insoluble sulphide.)

$$ZnSO_4 + (NH_4)_2S = (NH_4)_2SO_4 + ZnS.$$

2. From neutral zinc solutions, or from solutions containing free acetic acid, hydrogen sulphide precipitates white zinc sulphide.

3. Add ammonium, sodium, or potassium hydroxide: a white precipitate of zinc hydroxide, $Zn(OH)_2$, is produced, soluble in excess of the reagent, with the formation of zincates, such as $Zn(OK)_2$.

4. Soluble carbonates and phosphates give white precipitates in neutral solutions of zinc.

5. Potassium ferrocyanide gives a white precipitate of zinc ferrocyanide. (This test may be used to distinguish compounds of zinc from those of magnesium or aluminum.)

6. Zinc is the *only* heavy metal whose compounds are all colorless. The oxide, carbonate, phosphate, and ferrocyanide are insoluble; the chloride, nitrate, and sulphate soluble.

Cadmium, Cd = 111.5. Found in nature associated (though in very small quantities) with the various ores of zinc, with which metal it has in common a number of physical and chemical properties. Cadmium differs from zinc by forming a yellow sulphide (with hydrosulphuric acid), insoluble in diluted acids. Cadmium and its compounds are of little interest here; the yellow sulphide is used as a pigment, the sulphate and iodide sometimes for medicinal purposes.

QUESTIONS.—261. How is zinc found in nature, and by what process is it obtained? 262. Mention the properties of metallic zinc, and what is it used for? 263. Mention two processes for making zinc oxide. 264. How does heat act on zinc oxide? 265. Show by chemical symbols the action of hydrochloric and sulphuric acids on zinc. 266. State the properties of chloride and of sulphate of zinc? 267. What is white vitriol? 268. Explain the formation of precipitated zinc carbonate, and state its composition. 269. Mention tests for zinc compounds. 270. How many pounds of crystallized zinc sulphate may be obtained from 21.7 pounds of metallic zinc?

Summary of analytical characters of metals of the iron group.

	Ferrous salts.	*Ferric salts.*	*Manganese.*	*Zinc.*	*Cobalt.*	*Nickel.*
Ammonium sulphide	Black precipitate.	Black precipitate.	Flesh-colored precipitate.	White precipitate.	Black precipitate.	Black precipitate.
Ammonia water	Dirty green precipitate.	Reddish-brown precipitate.	White precipitate.	White precipitate.	Blue precipitate	Green precipitate.
In excess of reagent . . .	Insoluble.	Insoluble	Soluble.	Soluble.	Soluble.	Soluble.
Sodium hydroxide	Dirty green precipitate	Reddish-brown precipitate.	White precipitate.	White precipitate.	Blue precipitate	Green precipitate.
In excess of reagent . . .	Insoluble.	Insoluble.	Insoluble.	Soluble.	Insoluble.	Insoluble.
Sodium carbonate	White precipitate, turning dark.	Reddish-brown precipitate.	White precipitate, turning darker.	White precipitate.	Blue precipitate	Green precipitate.
Ammonium carbonate . . .	White precipitate, darkens.	Reddish-brown precipitate.	White precipitate, darkens	White precipitate.	Blue precipitate.	Green precipitate.
In excess of reagent . . .	Insoluble.	Insoluble.	Insoluble.	Soluble.	Soluble.	Soluble.
Potassium ferrocyanide . . .	Pale blue precipitate turning darker.	Dark blue precipitate.	White precipitate.	White precipitate.	Grayish-green precipitate.	Greenish-white precipitate
Potassium ferricyanide . . .	Dark blue precipitate.	No precipitate, greenish brown color.	Pale brown precipitate.	Pale brownish-yellow precipitate.	Deep brown-red precipitate	Yellowish-brown precipitate
Potassium sulphocyanate . . .	....	Dark red color.	....	....	Color much intensified.	Green color slightly intensified.
Borax bead in oxidizing flame	....	Dark yellow to red, while hot	Violet.	....	Blue.	Red, while hot.

28. LEAD–COPPER–BISMUTH.

General remarks regarding the metals of the lead group. The six metals belonging to this group (Pb, Cu, Bi, Ag, Hg, and Cd) are distinguished by forming sulphides which are insoluble in water, insoluble in dilute mineral acids, insoluble in ammonium sulphide; consequently they are precipitated from neutral, alkaline, or acid solutions by hydrogen sulphide or ammonium sulphide.

The metals themselves do not decompose water at any temperature, and are not acted upon by dilute sulphuric acid; heated with strong sulphuric acid, most of these metals are converted into sulphates with liberation of sulphur dioxide; nitric acid converts all of them into nitrates with liberation of nitrogen dioxide.

The oxides, iodides, sulphides, carbonates, phosphates, and a few of the chlorides and sulphates of these metals are insoluble; all the nitrates, and most of the chlorides and sulphates are soluble.

In regard to valence, they show no uniformity whatever, silver being univalent, copper, cadmium, and mercury bivalent, bismuth trivalent, and lead either bivalent or quadrivalent.

Lead, $Pb^{ii} = 206.4$ (*Plumbum*). This metal is obtained almost exclusively from the native sulphide of lead, called *galena*, PbS, by roasting until it is converted into oxide, and smelting this with coke in a blast furnace.

Lead owes its usefulness in the metallic state chiefly to its softness, fusibility, and resistance to acids, which properties are of advantage in using it for tubes or pipes, or in constructing vessels to hold or manufacture sulphuric acid. Lead is a constituent of many alloys, as, for instance, of type-metal, solder, britannia metal, shot, etc.

Experiment 31. Dissolve 1 gramme of lead acetate or lead nitrate in about 200 c.c. of water, suspend in the centre of the solution a piece of metallic zinc and set aside. Notice that metallic lead is deposited slowly upon the zinc in a crystalline condition, whilst zinc passes into solution, which may be verified by analytical methods. The chemical change taking place is this:

$$Pb(NO_3)_2 + Zn = Zn(NO_3)_2 + Pb.$$

The formation of the crystallized lead is called generally a lead-tree.

Lead oxide, Plumbi oxidum, $PbO = 222.4$ (*Litharge*). Obtained by exposing melted lead to a current of air, when the metal is gradually oxidized with the formation of a yellow powder, known as *massicot;* at a high temperature this fuses, forming reddish-yellow crystalline scales, known as *litharge;* by heating still further in contact with air, a portion of the oxide is converted into dioxide (or peroxide), PbO_2, and a red powder is formed, known as *red lead* (or *minium*), which probably is a mixture (or combination) of oxide and dioxide of lead, $PbO_2(PbO)_2$.

Lead oxide is used in the manufacture of lead salts, lead plaster, glass, paints, etc.

Nitric acid when heated with red lead combines with the oxide, while *lead dioxide*, PbO_2, is left as a dark-brown powder, which, on heating with hydrochloric acid, evolves chlorine (similar to manganese dioxide).

Lead nitrate, Plumbi nitras, $Pb(NO_3)_2 = 330.4$. Obtained by dissolving the oxide in nitric acid:

$$PbO + 2HNO_3 = H_2O + Pb(NO_3)_2.$$

Lead nitrate is the only salt of lead (with a mineral acid) which is easily soluble in water; it has a white color, and a sweetish, astringent, and afterward metallic taste.

Lead carbonate, Plumbi carbonas, $2(PbCO_3).Pb(OH)_2 = 773.2$ (*White-lead*). This compound may be obtained by precipitation of lead nitrate with sodium carbonate, but is manufactured on a large scale directly from lead, by exposing it to the simultaneous action of air, carbon dioxide, and vapors of acetic acid. The latter combines with the lead, forming a basic acetate, which is converted into the carbonate (almost as soon as produced) by the carbon dioxide present.

The action of acetic acid on lead or lead oxide will be considered in connection with acetic acid.

Lead carbonate is a heavy, white, insoluble, tasteless powder; the white-lead of commerce frequently is found adulterated with barium sulphate.

Lead iodide, Plumbi iodidum, $PbI_2 = 459.4$ (*Iodide of lead*). Made by adding solution of potassium iodide to lead nitrate (Plate III., 6):

$$Pb(NO_3)_2 + 2KI = 2KNO_3 + PbI_2.$$

It is a heavy, bright yellow, almost insoluble powder, which may be distinguished from lead chromate by its solubility in ammonium chloride solution on boiling, lead chromate being insoluble in this solution.

Poisonous properties and antidotes. Compounds of lead are directly poisonous, and it happens, not infrequently, that water passing through leaden pipes or collected in leaden tanks becomes contaminated with lead. Water free from air and salts scarcely acts on lead; but if it contain air, oxide of lead is formed, which is either dissolved by the water or is decomposed by the nitrates or chlorides present in the water, the soluble nitrate or chloride of lead being formed.

If the water contains carbonates and sulphates, however, these will form insoluble compounds, producing a film or coating over the lead, preventing further contact with the water. Rain water, in consequence of its containing atmospheric constituents, and no sulphates, acts as a solvent on lead pipe; spring and river waters generally do not.

Water containing lead will show a dark color on passing hydrogen sulphide through it; if the quantity present be very small, the water should be evaporated to $\frac{1}{10}$ or even $\frac{1}{100}$ of its original volume before applying the test.

The constant handling of lead compounds is one of the causes of lead poisoning (painters' colic). As an antidote, mangesium sulphate should be used, which forms with lead an insoluble sulphate; the purgative action of magnesia is also useful. (In lead works workmen often drink water containing a little sulphuric acid.)

Analytical reactions.

(Lead acetate or lead nitrate, $Pb(NO_3)_2$, may be used.)

1. To a solution of lead salt add hydrogen sulphide or ammonium sulphide: a black precipitate of lead sulphide is produced (Plate III., 1):

$$Pb(NO_3)_2 + H_2S = 2HNO_3 + PbS.$$

2. Add sulphuric acid or soluble sulphate: a white precipitate of lead sulphate is formed:

$$Pb(NO_3)_2 + Na_2SO_4 = 2NaNO_3 + PbSO_4.$$

3. Add hydrochloric acid or a soluble chloride: a white precipitate of lead chloride, $PbCl_2$, is produced, which dissolves on heating or on the addition of much water, as lead chloride is not entirely insoluble. For the same reason, the precipitate is not formed when the solutions used are highly dilute.

4. Other reagents which give precipitates with lead solutions are:

Potassium chromate, producing yellow lead chromate (chrome yellow). (Plate II., 6.)
Potassium iodide, producing yellow lead iodide. (Plate III., 6.)
Alkali carbonates, producing white basic lead carbonate.
Alkali phosphates, producing white lead phosphate

Copper, $Cu^{II} = 63.2$ (*Cuprum*). Found in nature sometimes in the metallic state—generally, however, combined with sulphur or oxygen.

The commonest copper-ore is *Copper pyrites*, a double sulphide of copper and iron, Cu_2FeS_2 or $Cu_2S.Fe_2S_3$, having the color and lustre of brass or gold. Other ores are: *Copper glance*, cuprous sulphide, having a dark-gray color and the composition Cu_2S; *malachite*, a beautiful green mineral, being a carbonate and hydroxide of copper, $CuCO_3.Cu(OH)_2$. Cuprous and cupric oxide also are found occasionally. Copper is obtained from the oxide by reducing it with coke; sulphides previously are converted into oxide by roasting.

Copper is the only metal showing a distinct red color; it is so malleable that, of the metals in common use, only gold and silver surpass it in that respect; it is one of the best conductors of heat and electricity, it does not change in dry air, but becomes covered with a film of green subcarbonate when exposed to moist air.

Copper frequently is used in the manufacture of alloys, of which the more important are:

	Copper.	*Zinc.*	*Tin.*	*Nickel.*
Brass	64	36	...	...
German silver	51	31	...	18
Bell-metal	78	...	22	...
Bronze	80	16	4	...
Gun-metal	90	...	10	...

Copper frequently is alloyed with gold and silver.

Copper is a bivalent element, forming two oxides and two series of salts, distinguished as cuprous and cupric compounds; the cuprous salts are here but of little interest.

Cupric oxide, CuO (*Black oxide or monoxide of copper*). Heated to redness, copper becomes covered with a black scale, which is cupric oxide; it is obtained also by heating cupric nitrate or carbonate, both compounds being decomposed with formation of the oxide; finally, it may be made by adding sodium or potassium hydroxide to the solution of a cupric salt, when a bulky, pale-blue precipitate of *cupric hydroxide*, $Cu(OH)_2$, is formed, which, upon boiling, is decomposed into water and cupric oxide, a heavy dark-brown powder (Plate III., 2):

$$CuSO_4 + 2KOH = K_2SO_4 + Cu(OH)_2;$$
$$Cu(OH)_2 = H_2O + CuO.$$

Cuprous oxide, Cu_2O (*Red oxide or suboxide of copper*). When cupric oxide is heated with metallic copper, charcoal, or organic matter, the cupric oxide is decomposed, and cuprous oxide is formed. (Excess of carbon or organic matter reduces the oxide to metallic copper.)

$$CuO + Cu = Cu_2O;$$
$$2CuO + C = Cu_2O + CO.$$

Some organic substances, especially grape-sugar, decompose alkaline solutions of cupric sulphate with precipitation of cuprous oxide, which is a red, insoluble powder.

Cupric sulphate, Cupri sulphas, $CuSO_4.5H_2O = 249.2$ (*Sulphate of copper, Blue vitriol, Blue-stone*). This is the most important compound of copper. It is manufactured on a large scale, either from copper pyrites, or by dissolving cupric oxide in sulphuric acid, evaporating and crystallizing the solution :

$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$

Cupric sulphate forms large, transparent, deep-blue crystals, which are easily soluble in water, and have a nauseous, metallic taste. By heating it to about 200° C. (392° F.) all water of crystallization is expelled, and the *anhydrous cupric sulphate* formed, which is a white powder. By further heating this is decomposed, sulphuric and sulphurous oxides are evolved, and cupric oxide is left.

Experiment 32. Boil about 5 grammes of fine copper wire with 15 c.c. of concentrated sulphuric acid until the action ceases and most of the copper is dissolved. Dilute with about 15 c.c. of hot water, filter, and set aside for crystallization. State the exact quantities of copper and H_2SO_4 required to make 100 pounds of crystallized cupric sulphate.

Cupric carbonate is obtained by the addition of sodium carbonate to solution of cupric sulphate, when a bluish-green precipitate is formed, which is cupric carbonate with hydroxide (Plate III., 4); by dissolving this in the various acids, the different cupric salts are obtained.

Ammonio-copper compounds. A number of compounds are known which are either double salts of ammonia and copper, or are derived from ammonium salts and contain copper. Thus, cupric chloride forms with ammonia the compounds: $CuCl_2(NH_3)_2$, $CuCl_2(NH_3)_4$, and $CuCl_2(NH_3)_6$. Cupric sulphate forms in like manner, cupric-diammonium sulphate, $CuSO_4(NH_3)_2$, and cupric tetrammonium sulphate, $CuSO_4(NH_3)_4$, which is a deep azure-blue compound taking up one molecule of water during crystallization.

It is this formation of soluble ammonio-copper compounds which causes the deep blue color in solutions of cupric salts on the addition of ammonia water.

Poisonous properties and antidotes. The use of copper for culinary vessels is frequently the cause of poisoning by this metal. A perfectly clean surface of metallic copper is not affected by any of the substances used in the preparation of food, but as the metal is very apt to become covered with a film of oxide when exposed to the air, and as the oxide is easily dissolved by the combined action of water, carbonic or other acids, such as are found in vinegar, the juice of fruits, or rancid fats, the use of copper for culinary vessels is always dangerous. Actual adulterations of food with compounds of copper have been detected.

In cases of poisoning by copper the stomach-pump should be used, vomiting induced, and albumen (white of egg) administered, which forms an insoluble compound with copper. Reduced iron, or a very dilute solution of potassium ferrocyanide, may be of use as antidotes.

Analytical reactions.

(Cupric sulphate, $CuSO_4$, may be used.)

1. Add to solution of copper, hydrogen sulphide or ammonium sulphide : a black precipitate of cupric sulphide is formed. (Plate III., 1):

$$CuSO_4 + H_2S = H_2SO_4 + CuS.$$

2. Add sodium or potassium hydroxide: a bluish precipitate of cupric hydroxide, $Cu(OH)_2$, is formed which is converted into dark-brown cupric oxide, CuO, by boiling. (See equation above.) (Plate III., 2.)

3. Add ammonium hydroxide: a bluish precipitate of cupric hydroxide is formed which readily dissolves in an excess of the reagent, forming a deep azure-blue solution containing an ammonio-copper compound. (See explanation above.) (Plate III., 3.)

4. Add potassium ferrocyanide: a reddish-brown precipitate of cupric ferrocyanide, $Cu_2Fe(CN)_6$, is obtained. (Plate III., 5.)

5. Add solution of arsenous acid and carefully neutralize with sodium hydroxide : green cupric arsenite is precipitated. (Plate V., 2.)

6. Add sodium or potassium carbonate: green cupric carbonate with hydroxide is precipitated. (Plate III., 4.)

7. Immerse a piece of iron, or steel, showing a bright surface, in an acidified solution of copper: the latter is precipitated upon the iron, an equivalent amount of iron passing into solution:

$$CuSO_4 + Fe = FeSO_4 + Cu.$$

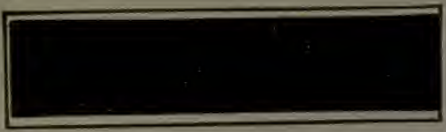
8. Most compounds of copper color the flame green, cupric chloride blue.

9. Cupric compounds give a blue, cuprous compounds a red borax bead.

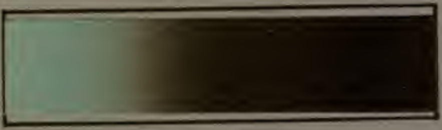
10. Cupric salts (when not anhydrous) have mostly a blue or green

PLATE III.

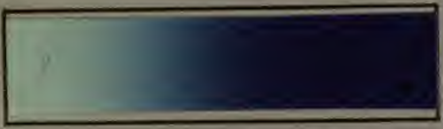
COPPER. LEAD. BISMUTH.

1 

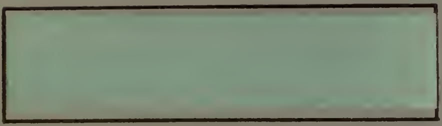
Cupric sulphide or lead sulphide, precipitated from solutions of copper or lead by hydrogen sulphide.

2 

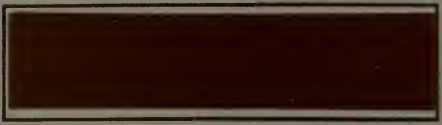
Cupric hydroxide passing into **cupric oxide.** Cupric solutions precipitated by potassium hydroxide and boiling.

3 

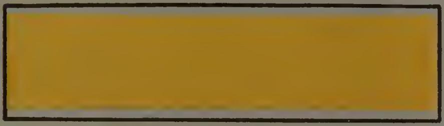
Cupric solutions treated with ammonia water.

4 

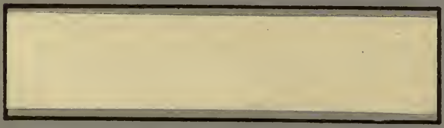
Cupric carbonate, precipitated from cupric solutions by sodium carbonate.

5 

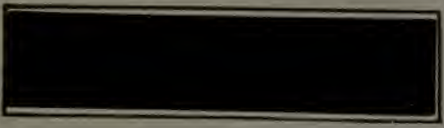
Cupric ferrocyanide, precipitated from cupric solutions by potassium ferrocyanide.

6 

Lead iodide, precipitated from lead solutions by soluble iodides.

7 

Lead solutions with soluble chlorides, sulphates or carbonates. **Bismuth solutions** with alkali hydroxides or carbonates.

8 

Bismuth sulphide, precipitated from bismuth solutions by hydrogen sulphide.

color: sulphate, nitrate, chloride, and the ammonio-copper compounds are soluble, most other compounds are insoluble.

Bismuth, $Bi^{iii} = 208.9$. Found in nature chiefly in the metallic state, disseminated, in veins, through various rocks. The extraction of the metal is a mere mechanical process, the earthy matter containing it being heated in iron cylinders, and the melted bismuth collected in suitable receivers.

Bismuth is grayish-white, with a pinkish tinge, very brittle, generally showing a distinct crystalline structure. Occasionally it is used in alloys and in the manufacture of a few medicinal preparations.

Bismuth is trivalent, as shown in the chloride, $BiCl_3$, or oxide, Bi_2O_3. A characteristic property of this metal is decomposition of the concentrated solution of any of its normal salts by the addition of much water, with the formation and precipitation of so-called oxysalts or subsalts of bismuth, while some bismuth with a large quantity of acid remains in solution.

The true constitution of these subsalts is as yet doubtful, but a comparison of them has led to the assumption of a radical *Bismuthyl*, BiO, which behaves like an atom of a univalent metal.

The relation between the normal or bismuth salts, and the subsalts or bismuthyl salts, will be shown by the composition of the following compounds:

Bismuth chloride,	$BiCl_3$.	Bismuthyl chloride,	$(BiO)Cl$.
" bromide,	$BiBr_3$.	" bromide,	$(BiO)Br$.
" iodide,	BiI_3.	" iodide,	$(BiO)I$.
" nitrate,	$Bi(NO_3)_3$.	" nitrate,	$(BiO)NO_3$.
" sulphate,	$Bi_2(SO_4)_3$.	" sulphate,	$(BiO)_2SO_4$.
" carbonate,	$Bi_2(CO_3)_3$ not known.	" carbonate,	$(BiO)_2CO_3$.

Bismuthyl nitrate, Bismuth subnitrate, Bismuthi subnitras, $BiONO_3.H_2O$? (*Oxynitrate of bismuth*). By dissolving metallic bismuth in nitric acid, a solution of bismuth nitrate is obtained, nitrogen dioxide escaping:

$$Bi + 4HNO_3 = Bi(NO_3)_3 + NO + 2H_2O.$$

Upon evaporation of the solution, colorless crystals of *bismuth nitrate*, $Bi(NO_3)_35H_2O$, are obtained.

If, however, the solution (or the dissolved crystals) be poured into a large quantity of water, the salt is decomposed with the formation of bismuthyl nitrate and nitric acid, which latter keeps in solution some bismuth:

$$Bi(NO_3)_3 + 2H_2O = BiONO_3.H_2O + 2HNO_3.$$

Subnitrate of bismuth is a heavy, white, tasteless powder, almost insoluble in water, soluble in most acids.

Experiment 33. Dissolve by the aid of heat about 1 gramme of metallic bismuth in a mixture of 2 c.c. of nitric acid and 1 c.c. of water. Evaporate the clear solution to about one-half its volume, in order to remove excess of acid, and pour this solution of normal bismuth nitrate into 100 c.c. of water. Collect the precipitate of bismuthyl nitrate on a filter, wash and dry it. Prove the presence of bismuth in the filtrate by tests mentioned below.

Bismuthyl carbonate, Bismuth subcarbonate, Bismuthi subcarbonas, $(BiO)_2CO_3.H_2O$ (?) (*Oxycarbonate of bismuth, Pearl-white*). Made by adding sodium carbonate to solution of bismuth nitrate, when the subcarbonate is precipitated, some carbon dioxide escaping:

$$2[Bi(NO_3)_3] + 3Na_2CO_3 + H_2O = 6NaNO_3 + 2CO_2 + (BiO)_2CO_3.H_2O.$$

A white, or pale yellowish-white powder, resembling the subnitrate. It readily loses water and carbon dioxide on heating, when the *yellow oxide*, Bi_2O_3, is left.

Bismuthyl iodide, Bismuth subiodide, BiOI, may be obtained by adding solution of hydriodic acid to freshly precipitated bismuth oxide:

$$Bi_2O_3 + 2HI = 2BiOI + H_2O.$$

A better method for making the compound is to pour gradually a solution, made by dissolving 95 grammes of crystallized normal bismuth nitrate in 125 c.c. of glacial acetic acid, into a solution of 40 grammes of potassium iodide, and 55 grammes of sodium acetate in 2500 c.c. of water. The precipitate, which has a brick-red color, is well washed and dried at 100° C. (212° F.). The decomposition is this:

$$\begin{aligned}2[Bi(NO_3)_3] &+ 2H_2O + 2KI + 4NaC_2H_3O_2 = \\ 2(BiOI) &+ 4NaNO_3 + 2KNO_3 + 4C_2H_4O_2.\end{aligned}$$

Analytical reactions.

(Bismuth nitrate, $Bi(NO_3)_3$, or bismuth chloride, $BiCl_3$, may be used.)

1. Add to solution of bismuth, hydrogen sulphide or ammonium sulphide: a dark-brown (almost black) precipitate of bismuth sulphide, Bi_2S_3, is produced (Plate III., 8):

$$2BiCl_3 + 3H_2S = 6HCl + Bi_2S_3.$$

2. Pour a concentrated solution of bismuth into water: a white precipitate of a bismuthyl salt is formed. (See explanation above.)

3. Add to bismuth solution ammonium or sodium hydroxide, or carbonate: a white precipitate of bismuth hydroxide, $Bi(OH)_3$, or of bismuthyl carbonate is produced. (See explanation above.)

4. Potassium iodide precipitates brown bismuth iodide, BiI_3, soluble in excess of the reagent.

5. Potassium dichromate precipitates yellow bismuthyl dichromate, $(BiO)_2Cr_2O_7$.

6. A small quantity of bismuth or of any bismuth compound, mixed with sulphur and potassium iodide, and heated upon charcoal before the blow-pipe, forms a scarlet-red incrustation of bismuthyl iodide, BiOI.

29. SILVER—MERCURY.

Silver, Ag = 107.7 (*Argentum*). This metal is found sometimes in the metallic state, but generally as a sulphide, which is nearly always in combination with large quantities of lead sulphide, such ore being known as *argentiferous galena*. The lead manufactured from this ore contains the silver, and is separated from it by roasting the alloy in a current of air, whereby lead is oxidized and converted into litharge, while pure silver is left.

Silver is the whitest of all metals, and takes the highest polish; it is the best conductor of heat and electricity, and melts at about 1000° C. (1832° F.); it is univalent, and forms but one series of salts; it is not affected by the oxygen of the air at any temperature, but is readily acted upon by traces of hydrosulphuric acid, which forms a black film of sulphide upon the surface of metallic silver. Hydrochloric acid scarcely acts on silver, nitric and sulphuric acids dissolve it.

QUESTIONS.—271. What are the properties of lead and from what ore is it obtained? 272. What is litharge, and how does it differ from red lead? 273. Give the composition of nitrate, carbonate, and iodide of lead; how are they made? 274. State the analytical reactions for lead. 275. How is copper found in nature? 276. How many oxides of copper are known; what is their composition, and under what conditions are they formed? 277. What is "blue vitriol;" how is it made, and what are its properties? 278. How does ammonium hydroxide act on cupric solutions? 279. Mention tests for copper. 280. What is the composition of subnitrate and subcarbonate of bismuth; how are they made from metallic bismuth, and what explanation is given in regard to their constitution?

While many of the non-metallic elements have long been known to exist in allotropic forms, none of the metals had been obtained in such a condition until quite recently, when it was shown that silver is capable of assuming a number of allotropic modifications. These are obtained chiefly by precipitating silver from solutions by different reducing agents. While normal silver is white, the allotropic forms have distinct colors—blue, bluish-green, red, purple, yellow—and differ also in many other respects. Thus they are converted into silver chloride by highly diluted hydrochloric acid, which does not act on common silver; they are soluble in ammonia water, and act as reducing agents upon a number of substances, such as permanganates, ferricyanides, etc. Allotropic silver can be converted into the common form by different forms of energy—for instance, by heat, electricity, and the action of strong acids.

Silver is too soft for use as coin or silverware, and, therefore, is alloyed with from 5 to 25 per cent. of copper, which causes it to become harder, and consequently gives it more resistance to the wear and tear by friction.

Pure silver may be obtained by dissolving silver coin in nitric acid, when a blue solution, containing the nitrates of copper and silver, is formed. By the addition of sodium chloride to the solution a white curdy precipitate of *silver chloride*, AgCl, forms, while cupric nitrate remains in solution. The silver chloride is washed, dried, mixed with sodium carbonate, and heated in a crucible, when sodium chloride is formed, carbon dioxide escapes, and a button of silver is found at the bottom of the crucible:

$$2AgCl + Na_2CO_3 = 2NaCl + CO_2 + 2Ag + O.$$

Experiment 34. Dissolve a small silver coin in nitric acid, dilute with water, and precipitate the clear liquid with an excess of solution of sodium chloride. The washed precipitate of silver chloride may be treated with sodium carbonate, as stated above, or may be converted into metallic silver by the following method: Place the dry chloride in a small porcelain crucible and apply a gentle heat until the chloride has fused; when cold, place a piece of sheet zinc upon the chloride, cover with water, to which a few drops of sulphuric acid have been added, and set aside for a day, when the silver chloride will be found to have been decomposed with liberation of metallic silver and formation of zinc chloride:

$$2AgCl + Zn = ZnCl_2 + 2Ag.$$

Wash the spongy silver with dilute sulphuric acid and then with water. Use this silver for making silver nitrate by dissolving it in nitric acid, and evaporation of the solution to dryness. Use this solution for silver reactions.

Silver nitrate, Argenti nitras, $AgNO_3 = 169.7$. Pure silver is dissolved in nitric acid:

$$3Ag + 4HNO_3 = NO + 2H_2O + 3AgNO_3.$$

The solution is evaporated to dryness with the view of expelling all free acid, the dry mass dissolved in hot water and crystallized.

If the silver used should contain copper, the latter may be eliminated from the mixture of silver and cupric nitrate by evaporating to dryness and fusing, when the latter salt is decomposed, insoluble cupric oxide being formed. The fused mass is dissolved in water, filtered, and again evaporated for crystallization.

When silver nitrate, after the addition of 4 per cent. of hydrochloric acid, is fused and poured into suitable moulds it yields the white cylindrical sticks which are known as *moulded silver nitrate, caustic, lunar caustic,* or *lapis infernalis.*

When fused with twice its weight of potassium nitrate and formed into similar rods, it forms the *diluted silver nitrate* (*mitigated caustic*) of the U. S. P.

Silver nitrate forms colorless, transparent, tabular, rhombic crystals, or, when fused, a white, hard substance; it is soluble in less than its own weight of water, the solution having a neutral reaction. Exposed to the light, especially in the presence of organic matter, silver nitrate blackens in consequence of decomposition; when brought in contact with animal matter, it is readily decomposed into free nitric acid and metallic silver, which produces the characteristic black stain; it is this decomposition, and the action of the free nitric acid, to which the strongly caustic properties of silver nitrate are due.

Nitrate of silver is used largely in photography, and also in the manufacture of various kinds of indelible inks and hair-dyes.

Silver oxide, Argenti oxidum, $Ag_2O = 231.4$. Made by the addition of an alkali hydroxide to silver nitrate:

$$2AgNO_3 + 2KOH = 2KNO_3 + H_2O + Ag_2O.$$

A dark-brown, almost black powder, but very sparingly soluble in water, imparting to the solution a weak alkaline reaction. It is a strong base, and easily decomposed into silver and oxygen.

Silver iodide, Argenti iodidum, $AgI = 234.3$. Made by the addition of potassium iodide to silver nitrate:

$$AgNO_3 + KI = KNO_3 + AgI.$$

A heavy, amorphous, light yellowish powder, insoluble in water, and but slightly soluble in ammonium hydroxide.

Antidotes. Sodium chloride, white of egg, or milk, followed by an emetic.

Analytical reactions.

(Silver nitrate, $AgNO_3$, may be used.)

1. Add to solution of a silver salt, hydrogen sulphide or ammonium sulphide: a dark-brown precipitate of silver sulphide is produced:

$$2AgNO_3 + H_2S = 2HNO_3 + Ag_2S.$$

2. Add hydrochloric acid, or any soluble chloride: a white, curdy precipitate of silver chloride is produced, which is insoluble in dilute acids, but soluble in ammonium hydroxide and in potassium cyanide.

$$AgNO_3 + NaCl = NaNO_3 + AgCl.$$

3. Add potassium chromate or dichromate: a red precipitate of silver chromate, Ag_2CrO_4, is formed (Plate II., 7).

4. Add sodium phosphate: a pale-yellow precipitate of silver phosphate, Ag_3PO_4, is formed, which is soluble in ammonia and in nitric acid.

5. Alkali hydroxides precipitate dark-brown silver oxide, soluble in ammonia water.

6. Potassium iodide or bromide gives a pale-yellow precipitate. (See above.)

7. Metallic copper, zinc, or iron precipitates metallic silver.

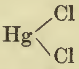
Mercury, Hydrargyrum, Hg = 199.8 (*Quicksilver*). Mercury is found sometimes in small globules in the metallic state, but generally as mercuric sulphide or *cinnabar*, a dark-red mineral. The chief supply was formerly obtained from Spain and Austria; now, however, large quantities are obtained from California; it is also imported from Peru and Japan.

Mercury is obtained from cinnabar either by roasting it, whereby the sulphur is converted into sulphur dioxide, or by heating it with lime, which combines with the sulphur, while the metal volatilizes, and is condensed by passing the vapors through suitable coolers.

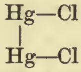
Mercury is the only metal showing the liquid state at the ordinary temperature; it solidifies at —40° C. (—40° F.), and boils at 357° C. (675° F.); but is slightly volatile at all temperatures; it is almost silver-white, and has a bright metallic lustre; its specific gravity is 13.56 at 15° C. (59° F.).

Mercury is peculiar in that its molecule contains but one atom, at least when in the state of a gas; in the liquid and solid states it may contain two atoms, like most other elements, but we have as yet no means of proving this fact.

Mercury is bivalent, and forms, like copper, two series of compounds, distinguished as mercuric and mercurous compounds. In the former, one atom of mercury exerts its bivalence, as in HgO, $HgCl_2$; in the mercurous compounds two atoms of mercury exert the same valence, as in Hg_2O, Hg_2Cl_2. In order to explain this behavior we have to assume that of the four points of attraction, represented by the two atoms of mercury, two are required to hold together or unite these two atoms, so as to leave but two for other elements.



Mercuric chloride.



$$\begin{array}{l} Hg-Cl \\ \;| \\ Hg-Cl \end{array}$$

Mercurous chloride.

There are known, however, some data which seem to contradict this view and make it not unlikely that the composition of mercurous chloride is $HgCl$, and not Hg_2Cl_2.

Mercury is not affected by the oxygen of the air, nor by hydrochloric acid, while chlorine, bromine, and iodine combine with it directly, and warm sulphuric and nitric acids dissolve it.

Mercury is used in the metallic state for many scientific instruments (thermometer, barometer, etc.); in the silvering of looking-glasses, which is effected by means of an amalgam of tin (amalgams are alloys in which mercury is one of the constituents); for manufacturing from it all of the various mercury compounds, and those official preparations in which mercury exists in the metallic state.

These latter preparations are: *Mercury with chalk*, *blue mass* or *blue pill*, *mercurial ointment*, and *mercurial plaster*. Mercury exists in a metallic, but highly subdivided state in these preparations, which are made by intimately mixing (triturating) metallic mercury with the different substances used (viz., chalk, pill-mass, fat, lead-plaster). It is most probable that the action of these agents upon the animal system is chiefly due to the conversion of small quantities of mercury into mercurous oxide, which, in contact with the acids of the gastric juice or with perspiration, are converted into soluble compounds capable of being absorbed.

Mercurous oxide, Hg_2O (*Black oxide or suboxide of mercury*). An almost black, insoluble powder, made by adding an alkaline hydroxide to a solution of mercurous nitrate:

$$Hg_2(NO_3)_2 + 2KOH = 2KNO_3 + H_2O + Hg_2O.$$

A similar decomposition takes place when alkaline hydroxides are added to insoluble mercurous chloride. A mixture of lime-water and mercurous chloride (calomel) is known as *black-wash;* when the two substances are mixed, calomel is converted into mercurous oxide, while calcium chloride is formed:

$$Hg_2Cl_2 + Ca(OH)_2 = CaCl_2 + H_2O + Hg_2O.$$

Mercuric oxide, HgO = 215.8. There are two mercuric oxides which are official; they do not differ in their chemical composition, but in their molecular structure.

The *yellow mercuric oxide, Hydrargyri oxidum flavum,* is made by pouring a solution of mercuric chloride into a solution of sodium hydroxide, when an orange-yellow, heavy precipitate is produced, which is washed and dried at a temperature not exceeding 30° C. (86° F.) (Plate IV., 3):

$$HgCl_2 + 2NaOH = HgO + 2NaCl + H_2O.$$

The *red mercuric oxide, Hydrargyri oxidum rubrum,* or *red precipitate,* is made by heating mercuric nitrate, either by itself or after it has been intimately mixed with an amount of metallic mercury equal to the mercury in the nitrate used (Plate IV., 4). In the first case, nitrous fumes and oxygen are given off, mercuric oxide remaining:

$$Hg(NO_3)_2 = HgO + 2NO_2 + O.$$

In the other case, no oxygen is evolved:

$$Hg(NO_3)_2 + Hg = 2HgO + 2NO_2.$$

The red oxide of mercury differs from the yellow oxide in being more compact, and of a crystalline structure; while the yellow oxide is in a more finely divided state, and consequently acts more energetically when used in medicine. Yellow oxide, when digested on a water-bath with a strong solution of oxalic acid, is converted into white mercuric oxalate within fifteen minutes, while red oxide is not acted upon by oxalic acid under the same conditions.

When mercuric chloride is added to lime-water, a mixture is formed holding in suspension yellow mercuric oxide; this mixture is known as *yellow-wash.*

Experiment 35. Heat some mercuric nitrate in a porcelain dish, placed in a fume chamber, until red fumes no longer escape. The remaining red powder is mercuric oxide, which, by further heating, may be decomposed into its elements.

Mercurous chloride, Hydrargyrum chloridum mite, Hg_2Cl_2 = 470.4 (*Calomel, Mild chloride of mercury, Subchloride or protochloride of mercury*). Mercurous chloride, like mercurous oxide, may be made by different processes, but the article used medicinally is the one obtained (except it be otherwise stated) by sublimation and the rapid condensation of the vapor in the form of powder.

It is made either by subliming a mixture of mercuric chloride and mercury:

$$HgCl_2 + Hg = Hg_2Cl_2.$$

or by thoroughly mixing with mercuric sulphate a quantity of mercury equal to that contained in the sulphate; by this operation mercurous sulphate is obtained, which is mixed with sodium chloride, and sublimed from a suitable apparatus into a large chamber, so that the sublimate may fall in powder to the floor:

$$HgSO_4 + Hg + 2NaCl = Na_2SO_4 + Hg_2Cl_2.$$

Precipitated calomel, being in a finer state of subdivision, acts more energetically when used medicinally. It is obtained by precipitation of a soluble mercurous salt by any soluble chloride:

$$Hg_2(NO_3)_2 + 2NaCl = 2NaNO_3 + Hg_2Cl_2.$$

Mercurous chloride, made by either process, generally contains traces of mercuric chloride, and should, therefore, be washed with hot water until the washings are no longer acted upon by ammonium sulphide or silver nitrate.

Mercurous chloride is a white, impalpable, tasteless powder, insoluble in water and alcohol; it volatilizes without fusing previously; when given internally, it should not be mixed with either mineral acids, alkali bromides, iodides, hydroxides, or carbonates, except the action of the decomposition products be desired.

Mercuric chloride, Hydrargyri chloridum corrosivum, $HgCl_2$ = 270.6 (*Corrosive chloride of mercury, Corrosive sublimate, Perchloride or bichloride of mercury*). Made by thoroughly mixing mercuric sulphate with sodium chloride, and subliming the mixture, when mercuric chloride is formed, and passes off in white fumes which are condensed in the cooler part of the apparatus, while sodium sulphate is left:

$$HgSO_4 + 2NaCl = Na_2SO_4 + HgCl_2.$$

Mercuric chloride is a heavy, white powder, or occurs in heavy, colorless, rhombic crystals or crystalline masses; it is soluble in 16 parts of cold and 2 parts of boiling water, and in about 3 parts of alcohol, in 4 parts of ether, and in about 14 parts of glycerin; when heated, it fuses and is volatilized; it has an acrid, metallic taste, an acid reaction, and strongly poisonous and antiseptic properties.

Mercurous iodide, Hydrargyri iodidum flavum, $Hg_2I_2 = 652.6$ (*Yellow iodide, green iodide, or protiodide of mercury*). Both iodides of mercury may be obtained either by rubbing together mercury and iodine in the proportions represented by the respective atomic weights, or by precipitation of soluble mercurous or mercuric salts by potassium iodide.

According to the U. S. P., mercurous iodide is made by the precipitation of a 4 per cent. solution of mercurous nitrate, to which 1 per cent. of nitric acid has been added, by a 2.4 per cent. solution of potassium iodide:

$$Hg_2(NO_3)_2 + 2KI = 2KNO_3 + Hg_2I_2.$$

The precipitate is collected on a filter, well washed with water and alcohol, and dried between paper at a temperature not exceeding 40° C. (104° F.). During the whole operation light should be excluded as much as possible, as it decomposes the compound.

Mercurous iodide is a yellow, tasteless powder, almost insoluble in water. It is easily decomposed into mercuric iodide and mercury, becoming darker and assuming a greenish-yellow tint. (Plate IV., 5.)

Mercuric iodide, Hydrargyri iodidum rubrum, $HgI_2 = 452.8$ (*Red iodide or biniodide of mercury*). Made by mixing solutions of potassium iodide and mercuric chloride, when a pale-yellow precipitate is formed, turning red immediately (Plate IV., 6):

$$HgCl_2 + 2KI = 2KCl + HgI_2.$$

Mercuric iodide is soluble both in solution of potassium iodide and mercuric chloride, for which reason an excess of either substance will cause a loss of the salt when prepared. It is a scarlet-red, tasteless powder, almost insoluble in water and but slightly soluble in alcohol; on heating or subliming it turns yellow in consequence of a molecular change which takes place; on cooling, and, more quickly, on pressing or rubbing the yellow powder, it reassumes the original condition and the red color.

Mercuric sulphate, $HgSO_4$. When mercury is heated with strong sulphuric acid (the presence of nitric acid facilitates the formation) chemical action takes place between the two substances, sulphur dioxide being liberated and mercuric sulphate formed, which is obtained as a heavy, white, crystalline powder:

$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2.$$

Yellow mercuric subsulphate, Hydrargyri subsulphas flavus, $HgSO_4.(HgO)_2 = 727.4$ (*Basic mercuric sulphate, Turpeth mineral, Mercuric oxy-sulphate*). When mercuric sulphate, prepared as directed above, is thrown into boiling water, it is decomposed into an acid salt which remains in solution, and a basic salt which is precipitated. As shown by its composition, $HgSO_4.(HgO)_2$, it may be looked upon as mercuric sulphate in combination with mercuric oxide. It is a heavy, lemon-yellow, tasteless powder, almost insoluble in water.

Mercurous sulphate, Hg_2SO_4. When mercuric sulphate is triturated with a sufficient quantity of mercury, direct combination takes place, and the mercurous salt is formed:

$$HgSO_4 + Hg = Hg_2SO_4.$$

Nitrates of mercury. *Mercurous nitrate,* $Hg_2(NO_3)_2$, and *Mercuric nitrate,* $Hg(NO_3)_2$, may both be obtained as white salts by dissolving mercury in nitric acid. The relative quantities of the two substances present determine whether mercurous or mercuric nitrate be formed. If mercury is present in excess the mercurous salt, if nitric acid is present in excess the mercuric salt, is formed, the latter especially on heating. Both salts are white and soluble in water.

Experiment 36. Heat gently a small globule (about 1 gramme) of mercury with 2 c.c. of nitric acid until red fumes cease to escape. If some of the mercury remains undissolved, the solution will deposit crystals of mercurous nitrate on cooling. Use some of the solution, after being diluted with much water, for mercurous tests. Use another portion as follows: Heat the solution, or some of the crystals, with about an equal weight of nitric acid until no more red fumes escape. Add to a few drops of the diluted liquid a little hydrochloric acid, which, if the conversion of the mercurous into mercuric salt has been complete, will give no precipitate. If, however, one should be formed, the solution is heated with more nitric acid until no precipitate is formed by hydrochloric acid, when the solution is evaporated and set aside for crystallization. The respective changes may be represented by the following equations:

$$6Hg + 8HNO_3 = 3[Hg_2(NO_3)_2] + 4H_2O + 2NO;$$
$$3[Hg_2(NO_3)_2] + 8HNO_3 = 6[Hg(NO_3)_2] + 4H_2O + 2NO.$$

Mercuric sulphide, $HgS = 231.8$. This compound has been mentioned as the chief ore of mercury, occurring crystallized as *cinnabar*, which has a *red* color (Plate IV., 2). The same compound may, however, be obtained by passing hydrosulphuric acid gas through mercuric solutions, when at first a white precipitate is formed (a double compound of the sulphide of mercury in combination with the mercuric salt), which soon turns *black* (Plate IV., 1):

$$HgCl_2 + H_2S = 2HCl + HgS.$$

The black, amorphous, mercuric sulphide may be converted into the red, crystallized variety by sublimation, and is then the preparation known as *red sulphide of mercury, cinnabar, or vermilion.* It forms brilliant dark-red crystalline masses, or a fine bright scarlet powder, which is insoluble in water, hydrochloric or nitric acid, but soluble in nitro-hydrochloric acid.

Mercuric and mercurous sulphides may be made also by triturating the elements mercury and sulphur in the proper proportions, when they combine directly.

Ammoniated mercury, Hydrargyrum ammoniatum, NH_2HgCl = 251.2 (*White precipitate, Mercuric-ammonium chloride*). This compound is made by pouring solution of mercuric chloride into water of ammonia, when a white precipitate falls, which is washed with highly diluted ammonia water and dried at a low temperature:

$$HgCl_2 + 2NH_4OH = NH_2HgCl + NH_4Cl + 2H_2O.$$

As shown by the composition of this compound, it may be regarded as ammonium chloride, NH_4Cl, in which two atoms of hydrogen have been replaced by one atom of the bivalent mercury. (There are many compounds known in which metallic atoms replace hydrogen in salts of ammonium; the ammonium copper compounds belong to this group of substances.)

Ammoniated mercury is a white, tasteless, insoluble powder.

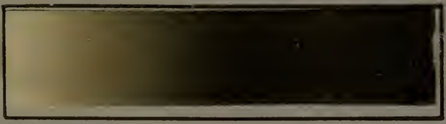
Analytical reactions.

	Mercurous salts. (Mercurous nitrate, $Hg_2(No_3)_2$ may be used.)	*Mercuric salts.* (Mercuric chloride, $HgCl_2$, may be used.)
1. Hydrogen sulphide, or ammonium sulphide.	Black precipitate of mercuric sulphide, with mercury. $Hg_2(NO_3)_2 + H_2S = 2HNO_3 + HgS + Hg$.	Black precipitate of mercuric sulphide. (Precipitate may be white or gray, with an insufficient quantity of the reagent.) (See above) (Plate IV., 1.)
2. Potassium iodide.	Green precipitate of mercurous iodide (Plate IV., 7): $Hg_2(NO_3)_2 + 2KI = 2KNO_3 + Hg_2I_2$.	Red precipitate of mercuric iodide (See above.) (Plate IV., 6.)
3. Potassium or sodium hydroxide.	Dark-brown precipitate of mercurous oxide, Hg_2O (Plate IV., 5).	Yellow precipitate of mercuric oxide HgO. (See above.) (Plate IV., 3.)
4. Ammonium hydroxide.	Black precipitate of mercurous ammonium salt is formed. (The insoluble white calomel is converted into a black powder.)	White precipitate of a mercuric ammonium salt is formed. (See explanation above.)
5. Potassium or sodium carbonate.	Yellowish precipitate of mercurous carbonate, which is unstable.	Brownish-red precipitate of basic mercuric carbonate. $HgCO_3.3HgO$.
6. Hydrochloric acid or soluble chlorides.	White precipitate of mercurous chloride is produced: $Hg_2(NO_3)_2 + 2HCl = 2HNO_3 + Hg_2Cl_2$.	No change

PLATE IV.

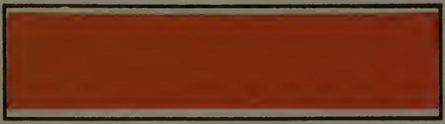
MERCURY. SILVER.

1



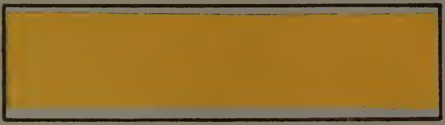
Mercuric sulphide, precipitated from mercuric solutions by hydrogen sulphide.

2



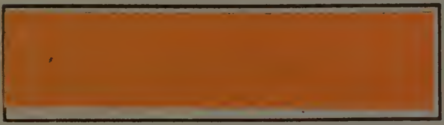
Mercuric sulphide, Cinnabar.

3



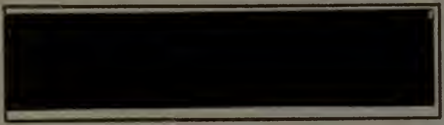
Yellow mercuric oxide, precipitated from mercuric solutions by potassium hydroxide.

4



Red mercuric oxide, obtained by heating mercuric nitrate.

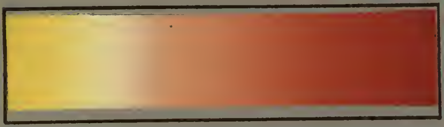
5



Mercurous oxide, precipitated from mercurous solutions by potassium hydroxide.

Silver sulphide, precipitated from silver solutions by hydrogen sulphide.

6

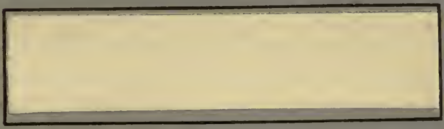


Mercuric iodide, precipitated from mercuric solutions by alkali iodides.

7

Mercurous iodide, precipitated from mercurous solutions by alkali iodides.

8



Mercuric solutions with ammonium hydroxide. **Mercurous solutions** with soluble chlorides. **Silver solutions** with soluble chlorides.

7. Stannous chloride produces, in solutions of mercury, a white precipitate, which turns dark-gray on heating with an excess of the reagent. The reaction is due to the strong reducing or deoxidizing property of the stannous chloride, which itself is converted into stannic chloride, while the mercury salt is first converted into a mercurous salt and afterward into metallic mercury:

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4;$$
$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4.$$

8. Dry mercury compounds, when mixed with sodium carbonate and potassium cyanide, and heated in a narrow test-tube, are decomposed with liberation of metallic mercury, which condenses in small globules in the cooler part of the tube.

9. A piece of bright metallic copper, when placed in a slightly acid mercury solution becomes coated with a dark film of metallic mercury, which by rubbing becomes bright and shining, and may be volatilized by heat.

10. All compounds of mercury are completely volatilized by heat, either with or without decomposition.

Antidotes. Albumen (white of egg), of which, however, not too much should be given at one time, lest the precipitate formed by the mercuric salt and albumin be redissolved. The antidote should be followed by an emetic to remove the albuminous mercury compound.

QUESTIONS.—281. How is silver obtained from the native ores, and how may it be prepared from silver coin? 282. State of silver nitrate: its composition, mode of preparation, properties, and names by which it is known. 283. Give analytical reactions for silver. 284. How is mercury found in nature; how is it obtained from the native ore; what are its physical and chemical properties? 285. Mention the three oxides of mercury; how are they made, what is their composition, what is their color and solubility? 286. State of the two chlorides of mercury: their names, composition, mode of preparation, solubility, color, and other properties. 287. Mention the same of the two iodides, as above, for the chlorides. 288. State the difference between mercuric sulphate, basic mercuric sulphate, and mercurous sulphate. 289. What is formed when ammonium hydroxide, calcium hydroxide, potassium or sodium hydroxide is added to either mercurous or mercuric chloride? 290. Give tests answering for any mercury compound, and tests by which mercuric compounds may be distinguished from mercurous compounds.

Summary of analytical characters of metals of the lead group.

	Lead.	*Copper.*	*Bismuth.*	*Silver.*	*Mercuric salts.*	*Mercurous salts.*	*Cadmium.*
Hydrogen sulphide	Black precipitate.	Black precipitate.	Dark-brown precipitate	Black precipitate.	Black precipitate.	Black precipitate.	Yellow precipitate.
Sodium hydroxide	White precipitate.	Blue precipitate turning brown on boiling.	White precipitate.	Brown precipitate.	Yellow precipitate.	Black precipitate.	White precipitate.
Ammonia water	White precipitate.	Pale-blue precipitate.	White precipitate.	Brown precipitate.	White precipitate.	Black precipitate.	White precipitate.
In excess of reagent	Insoluble	Dark blue solution.	Insoluble.	Colorless solution.	Insoluble.	Insoluble.	Colorless solution.
Sodium carbonate	White precipitate.	Greenish-blue precipitate.	White precipitate.	Pale-yellow precipitate.	Reddish-brown precipitate.	Yellowish precipitate.	White precipitate.
Potassium iodide	Yellow precipitate.	Yellow precipitate.	Brown precipitate.	Pale-yellow precipitate	Scarlet-red precipitate.	Yellowish-green precipitate.	....
In excess of reagent	Insoluble.	Insoluble.	Insoluble	Insoluble.	Soluble.	Partly soluble.	....
Potassium chromate	Yellow precipitate.	Orange precipitate.	....	Dark-red precipitate.	Orange precipitate.	Brick-red precipitate.	....
Hydrochloric acid	White precipitate, soluble in hot water.	....	....	White precipitate, soluble in ammonia water.	....	White precipitate, turning dark with ammonia.	....
Sulphuric acid	White precipitate.	....	....	....	....	White precipitate.	....

30. ARSENIC.

$As = 74.9$.

General remarks regarding the metals of the arsenic group. The metals belonging to either of the five groups considered heretofore, show much resemblance to each other in their chemical properties, and consequently in their combinations. This is much less the case among the six metals (As, Sb, Sn, Au, Pt, Mo) which are classed together in this group. In fact, the only resemblance which unites these metals is the insolubility of their sulphides in dilute acids and the solubility of these sulphides in ammonium sulphide (or alkali hydroxides), with which they form soluble double compounds; the oxides have also a tendency to form acids. In all other respects no general resemblance exists between these metals. Arsenic and antimony have many properties in common, and resemble in many respects the non-metallic elements phosphorus and nitrogen, as may be shown by a comparison of their hydrides, oxides, acids, and chlorides.

NH_3	N_2O_3	N_2O_5		NCl_3.
PH_3	P_2O_3	P_2O_5	H_3PO_4	PCl_3.
AsH_3	As_2O_3	As_2O_5	H_3AsO_4	$AsCl_3$.
SbH_3	Sb_2O_3	Sb_2O_5		$SbCl_3$.

Arsenic. Found in nature sometimes in the native state, but generally as sulphide or arsenide. One of the most common arsenic ores is the arsenio-sulphide of iron, or *mispickel*, FeSAs. *Realgar* is the native red sulphide, As_2S_2, and *orpiment* or *auripigment*, the native yellow sulphide, As_2S_3. Arsenides of cobalt, nickel, and other metals are not infrequently met with in nature. Certain mineral waters contain traces of arsenic compounds.

Arsenic may be obtained easily by heating arsenous oxide with charcoal, or by allowing vapors of arsenous oxide to pass over charcoal heated to redness:

$$As_2O_3 + 3C = 3CO + 2As.$$

In both cases the arsenic, when liberated by the reducing action of the charcoal, exists in the form of vapor, which condenses in the cooler part of the apparatus as a steel-gray metallic mass, which when exposed to the amospheric air, loses the metallic lustre in consequence of the formation of a film of oxide.

When pure, arsenic is odorless and tasteless; it is very brittle, and volatilizes unchanged and without melting when heated to 180° C.

(356° F.), without access of air. Heated in air, it burns with a bluish-white light, forming arsenous oxide. Although insoluble in water, yet water digested with arsenic soon contains some arsenous acid in solution, the oxide of arsenic being formed by oxidation of the metal by the oxygen absorbed in the water.

Arsenic is used in the metallic state as fly-poison, and in some alloys, chiefly in shot, an alloy of lead and arsenic.

The molecule of arsenic contains four atoms, and not two, like most elements. It is trivalent in some compounds, quinquivalent in others.

Arsenous oxide, Acidum arsenosum, $As_2O_3 = 197.8$ (*Arsenious oxide, White arsenic, Arsenic trioxide, Arsenous anhydride,* improperly *Arsenous acid*). This compound is frequently obtained as a by-product in metallurgical operations during the manufacture of metals from ores containing arsenic. Such ores are roasted (heated in a current of air), when arsenic is converted into arsenous oxide, which, at that temperature, is volatilized and afterward condensed in chambers or long flues.

Arsenous oxide is a heavy, white solid, occurring either as an opaque, slightly crystalline powder, or in transparent or semi-transparent masses which frequently show a stratified appearance; recently sublimed arsenous oxide exists as the amorphous semi-transparent glassy mass known as vitreous arsenous oxide, which gradually becomes opaque and ultimately resembles porcelain. This change is due to a rearrangement of the molecules into crystals which can be seen under the microscope.

The two modifications of arsenous oxide differ in their solubility in water, the amorphous or glassy variety dissolving more freely than the crystallized. One part of arsenous oxide dissolves in from 30 to 80 parts of cold and in 15 parts of boiling water, the solution having at first a faint acrid and metallic, and afterward a sweetish taste. This solution contains the arsenous oxide not as such, but as *arsenous acid*, H_3AsO_3, which compound, however, cannot be obtained in an isolated condition, but is known in solution only:

$$As_2O_3 + 3H_2O = 2H_3AsO_3.$$

A second arsenous acid, termed *met-arsenous acid* or *meta-arsenous acid*, $HAsO_2$, is known in some salts, as, for instance, in sodium met-arsenite, $NaAsO_2$, which salt may be obtained by the action of arsenous oxide on the carbonate, bicarbonate, or hydroxide of sodium:

$$As_2O_3 + 2NaOH = 2NaAsO_2 + H_2O.$$

When heated to about 218° C. (424° F.) arsenous oxide is volatilized without melting; the vapors, when condensed, form small, shining, eight-sided crystals; when heated on charcoal, it is deoxidized, giving off, at the same time, an odor resembling that of garlic.

Arsenous oxide is frequently used in the arts and for manufacturing purposes, as, for instance, in the manufacture of green colors, of opaque white glass, in calico-printing, as a powerful antiseptic for the preservation of organic objects of natural history, and, finally, as the substance from which all arsenic compounds are obtained.

The official *solution of arsenous acid, Liquor acidi arsenosi,* is a 1 per cent. solution of arsenous oxide in water to which 5 per cent. of diluted hydrochloric acid has been added.

The official *solution of arsenite of potassium, Liquor potassii arsenitis,* or *Fowler's solution,* is made by dissolving 1 part of arsenous oxide and 2 parts of potassium bicarbonate in 94 parts of water and adding 3 parts of compound tincture of lavender; the solution contains the arsenic as potassium met-arsenite.

Arsenic oxide, As_2O_5 (*Arsenic pentoxide, Anhydrous arsenic acid*). When arsenous oxide is heated with nitric acid, it becomes oxidized and is converted into *arsenic acid,* H_3AsO_4, from which the water may be expelled by further heating, when arsenic oxide is left:

$$2H_3AsO_4 = As_2O_5 + 3H_2O.$$

Arsenic oxide is a heavy, white, solid substance which, in contact with water, is converted into arsenic acid. This acid resembles phosphoric acid not only in composition, but also in forming metarsenic and pyroarsenic acid under the same conditions under which the corresponding phosphoric acids are formed. The salts of arsenic acid, the arsenates, also resemble in their constitution the corresponding phosphates.

Arsenic oxide and arsenic acid are used largely as oxidizing agents in the manufacture of aniline colors.

Disodium hydrogen arsenate, Sodii arsenas, $Na_2HAsO_4.7H_2O$ = 311.9 (*Sodium arsenate*). This salt is made by fusing arsenous oxide with carbonate and nitrate of sodium.

$$As_2O_3 + 2NaNO_3 + Na_2CO_3 = Na_4As_2O_7 + N_2O_3 + CO_2.$$

Sodium pyroarsenate is formed, nitrogen trioxide and carbon dioxide escaping. By dissolving in water and crystallizing, the official salt is obtained in colorless, transparent crystals:

$$Na_4As_2O_7 + 15H_2O = 2(Na_2HAsO_4.7H_2O).$$

Liquor sodii arsenatis is a 1 per cent. solution of sodium arsenate in water.

Hydrogen arsenide, AsH_3 (*Arsine, Arsenetted or arseniuretted hydrogen*). This compound is formed always when either arsenous or arsenic oxides or acids, or any of their salts, are brought in contact with nascent hydrogen, for instance, with zinc and diluted sulphuric acid, which evolve hydrogen:

$$As_2O_3 + 12H = 2AsH_3 + 3H_2O.$$
$$As_2O_5 + 16H = 2AsH_3 + 5H_2O.$$
$$AsCl_3 + 6H = AsH_3 + 3HCl.$$

Hydrogen arsenide is a colorless, highly poisonous gas, having a strong garlic odor. Ignited, it burns with a bluish flame, giving off white clouds of arsenous oxide:

$$2AsH_3 + 6O = As_2O_3 + 3H_2O.$$

When a cold plate (porcelain answers best) is held in the flame of arsenetted hydrogen, a dark deposit of metallic arsenic (arsenic spots) is produced upon the plate (in a similar manner as a deposit of carbon is produced by a common luminous flame). The formation of this metallic deposit may be explained by the fact that the heat of the flame decomposes the gas, and that, furthermore, of the two liberated elements, arsenic and hydrogen, the latter has the greater affinity for oxygen. In the centre of the flame, to which but a limited amount of oxygen penetrates, the latter is taken up by the hydrogen, arsenic being present in the metallic state until it burns in the outer cone of the flame. It is this liberated arsenic which is deposited upon a cold substance held in the flame.

Arsenetted hydrogen, when heated to redness, is decomposed into its elements; by passing the gas through a glass tube heated to redness, the liberated arsenic is deposited in the cooler part of the tube, forming a bright metallic ring.

Sulphides of arsenic. Two sulphides of arsenic are known and have been mentioned above as the native *disulphide or realgar*, As_2S_2, and the *trisulphide or orpiment*, As_2S_3. Disulphide of arsenic is an orange-red, fusible, and volatile substance, used as a pigment; it may be made by fusing together the elements in the proper proportions. Trisulphide is a golden-yellow, fusible, and volatile substance, which also may be obtained by fusing the elements, or by precipitating an arsenic solution by hydrogen sulphide (Plate V., 1). Both sulphides of arsenic are sulpho-acids, uniting with other metallic sulphides to form sulpho-salts, as, for instance, $K_2S.As_2S_3$, or $(NH_4)_2S.As_2S_3$. These compounds are known as sulph-arsenides.

Arsenous iodide, Arseni iodidum, $AsI_3 = 454.5$ (*Iodide of arsenic*), may be obtained by direct combination of the elements, and forms orange-red crystalline masses, soluble in water and alcohol, but decomposed by boiling with either of these liquids. It is used in the official preparation, *Solution of arsenic and mercuric iodide, Donovan's solution,* which is made by dissolving one part each of arsenous iodide and mercuric iodide in 98 parts of water.

Analytical reactions.

(Use arsenous oxide, As_2O_3, and sodium arsenate, Na_2HAsO_4, respectively.)

1. Add hydrogen sulphide to an aqueous solution of arsenous oxide: a yellow coloration but no precipitate is formed until some hydrochloric acid is added, when yellow arsenic trisulphide, As_2S_3 (Plate V., 1) is precipitated :

$$As_2O_3 + 3H_2S = 3H_2O + As_2S_3;$$

or

$$2H_3AsO_3 + 3H_2S = 6H_2O + As_2S_3.$$

When hydrogen sulphide is added to a cold solution of arsenic oxide or of an arsenate, acidified with hydrochloric acid, a yellow mixture of arsenic trisulphide, As_2S_3, and sulphur is slowly precipitated :

$$2H_3AsO_4 + 5H_2S = 8H_2O + As_2S_3 + 2S.$$

When the same substances act upon one another in hot solution, and when also an excess of hydrogen sulphide (preferably a current of the gas) is used, yellow arsenic pentasulphide is precipitated :

$$As_2O_5 + 5H_2S = 5H_2O + As_2S_5;$$

or

$$2H_3AsO_4 + 5H_2S = 8H_2O + As_2S_5.$$

2. Add ammonium sulphide or any alkali hydroxide to the yellow precipitate of arsenous or arsenic sulphide : the precipitates are readily dissolved, but may be reprecipitated by neutralizing with an acid.

3. Ammonio-nitrate of silver (silver nitrate to which enough of water of ammonia has been added to redissolve the precipitate at first formed) produces in neutral solutions of arsenous acid a *yellow* precipitate of silver arsenite, Ag_3AsO_3 (Plate V., 3); in arsenic acid solutions a *reddish-brown* precipitate of silver arsenate, Ag_3AsO_4 (Plate V., 4). The two precipitates are soluble in both alkalies and acids.

Silver arsenite dissolved in water of ammonia and boiled forms silver arsenate and metallic silver.

4. Ammonio-sulphate of copper (made similarly to ammonio-nitrate of silver from cupric sulphate) added to neutral arsenous solutions produces a green precipitate of cupric arsenite ($CuHAsO_3$) known as *Scheele's green* (Plate V., 2). (Arsenite of copper mixed with cupric acetate is known as *Schweinfurth green*). The same reagent produces in neutral solutions of an arsenate a similar green precipitate of cupric arsenate, $CuHAsO_4$. Cupric arsenite boiled with potassium hydroxide forms potassium arsenate and red cuprous oxide.

Instead of using for the above tests the ammonio salts, silver nitrate or cupric sulphate may be added to the acid (or neutral) solution of arsenic, then adding water of ammonia carefully in small quantities until a neutral reaction has been obtained, when the precipitate is formed.

5. Soluble arsenates give white precipitates with soluble salts of barium, calcium, magnesium, zinc, and some other metals; soluble arsenites do not. Arsenates give, on heating with ammonium molybdate, a yellow precipitate of ammonium arseno-molybdate, $(NH_4)_3AsO_4.10MoO_3$.

6. Heat any dry arsenic compound, after being mixed with some charcoal and dry potassium carbonate in a very narrow test-tube (or, better, in a drawn-out glass tube having a small bulb on the end): the arsenic compound is decomposed and the metallic arsenic deposited as a metallic ring in the upper part of the contraction. (Fig. 13.)

FIG. 13.

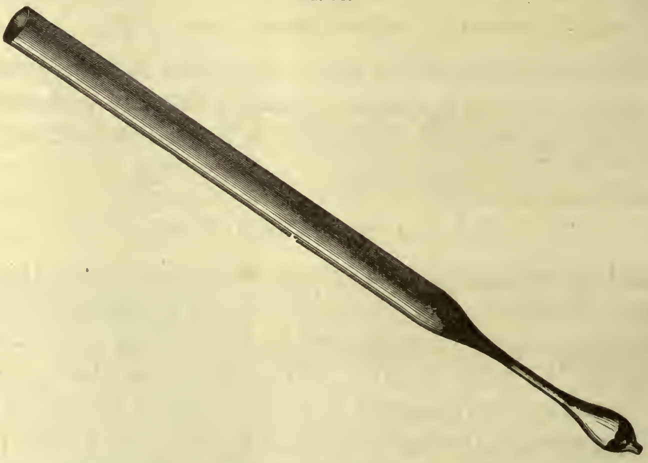
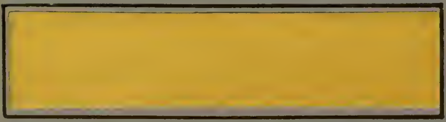


PLATE V.

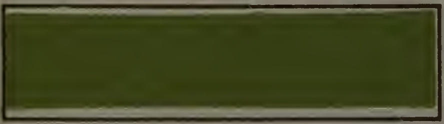
ARSENIC. ANTIMONY. TIN.

1



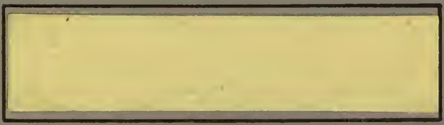
Arsenous sulphide, precipitated from arsenous solutions by hydrogen sulphide.

2



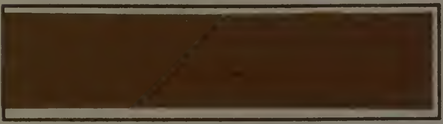
Cupric arsenite, precipitated from arsenous solutions by cupric-ammonium sulphate.

3



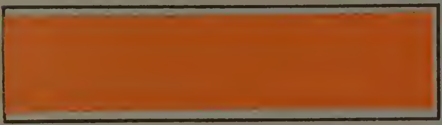
Silver arsenite, precipitated from arsenous solutions by silver nitrate.

4



Silver arsenate, precipitated from arsenic solutions by silver nitrate.

5

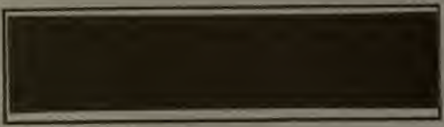


Antimonous sulphide, precipitated from solutions of antimony by hydrogen sulphide.

6

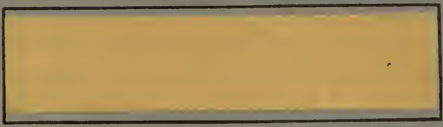
Native or **crystallized antimonous sulphide.**

7



Stannous sulphide, precipitated from stannous solutions by hydrogen sulphide.

8



Stannic sulphide, precipitated from stannic solutions by hydrogen sulphide.

7. Heat arsenous or arsenic oxide upon a piece of charcoal by means of a blowpipe; a characteristic odor of garlic is perceptible.

8. *Reinsch's test.* A thin piece of copper, having a bright metallic surface, placed in a slightly acidified solution of arsenic becomes, upon heating the solution, coated with a dark steel-gray deposit of arsenic, which can be vaporized by application of heat.

9. *Bettendorff's test.* Add to any arsenic compound, dissolved in concentrated hydrochloric acid, an equal volume of freshly prepared solution of stannous chloride in hydrochloric acid, add a small piece of tin-foil, and apply heat: a brown color or precipitate is formed, due to the separation of arsenic.

10. *Gutzeit's test.* Place a small piece (about 1 gramme) of pure zinc in a test-tube, add about 5 c.c. of dilute (5 per cent.) sulphuric acid and a few drops of any arsenic solution, which should not be alkaline. Fasten over the mouth of the test-tube a cap made of three thicknesses of pure filter paper, and moisten the upper paper with a drop of a saturated solution of silver nitrate in water, acidulated with about 1 per cent. of nitric acid. (Fig. 14.) Place the tube in a box so as to exclude all light, and examine the paper cap after awhile. Upon it will appear a bright yellow stain, rapidly if the quantity of arsenic be considerable, slowly if it be small. Upon moistening the yellow stain with water the color changes to brown or black. The action of hydrogen arsenide upon silver nitrate in the absence of water takes place with the formation of a yellow compound, thus:

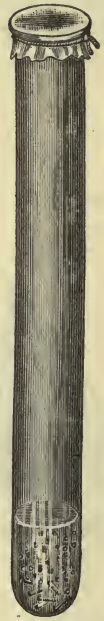
$$AsH_3 + 6AgNO_3 = 3HNO_3 + Ag_3As.(AgNO_3)_3.$$

In the presence of water metallic silver is separated, showing a black or brown color:

$$AsH_3 + 6AgNO_3 + 6H_2O = 6HNO_3 + H_3AsO_3 + 6Ag.$$

Compounds of antimony treated in the above manner produce a dark spot upon the paper, but cause no previous yellow color.

FIG. 14.



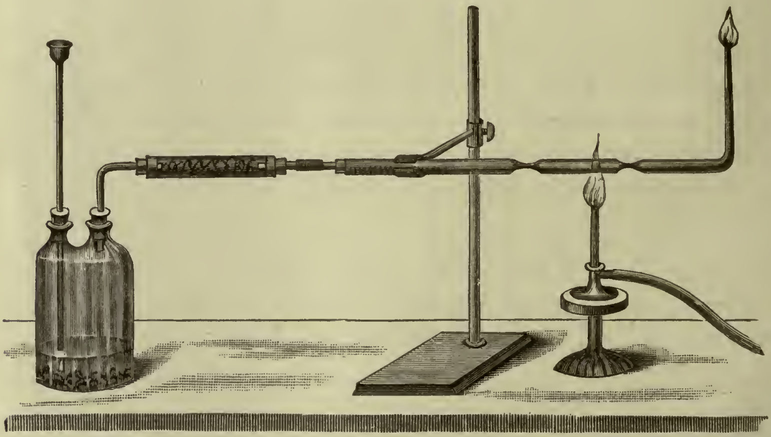
11. *Fleitmann's test.* This is similar to the previous test, the chief difference being that hydrogen is evolved in alkaline solution, which has the advantage that the presence of antimony does not interfere, because this metal does not form antimonetted hydrogen in alkaline solutions.

Place about 1 gramme of pure zinc in a test-tube, add about 5 c.c.

of potassium hydroxide solution and a few drops of the arsenic solution, which should not be acid. Provide paper cap as described in previous test, and set the test-tube in a box containing sand heated to about 90° C. (194° F.). A brown or black stain of metallic silver will appear upon the paper.

12. *Marsh's test.* While this test is not used now for qualitative determinations as much as formerly, it is of great value because it may serve for collecting the total amount of arsenic present in a specimen, thus permitting quantitative estimation. The apparatus (Fig. 15) used for performing this test consists of a glass vessel (flask or Woulf's bottle) provided with a funnel-tube and delivery-tube (bent at right angles), which is connected with a wider tube, filled with pieces of calcium chloride or plugs of asbestos; this drying-tube is again connected with a piece of hard glass tube, about one foot long, having a diameter of $\frac{1}{4}$ inch, drawn out at intervals of about 3 inches, so as to reduce its diameter to $\frac{1}{8}$ inch. Hydrogen is generated in the flask by the action of sulphuric acid on zinc, and examined for its purity by heating the glass tube to redness at one of its wide parts for at least 30 minutes; if no trace of a metallic mirror is formed at the constriction beyond the heated point, the gas and the substances used for its generation may be pronounced free from arsenic. (Both zinc and sulphuric acid often contain arsenic.)

FIG. 15.



Marsh's apparatus for detection of arsenic.

After having thus demonstrated the purity of the hydrogen, the suspected liquid, which must contain the arsenic either as oxide or chloride (not as sulphide), is poured into the flask through the funnel-tube. If arsenic is present in not too small quantities, the gas ignited at the end of the glass tube shows a flame decidedly different from that of burning hydrogen. The flame becomes larger, assumes a bluish tint, and emits an odor of garlic, while above it a white cloud appears which is more or less dense; a cold test-tube held inverted over the flame will be covered upon its walls with a white deposit of minute octahedral crystals of arsenous oxide; a piece of cold porcelain held in the flame becomes coated with a brown stain (arsenic spot) of metallic arsenic. (See explanation above in connection with arsenetted hydrogen.)

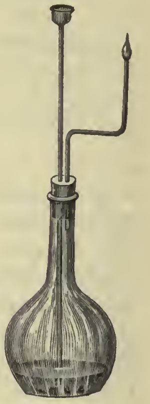
The glass tube heated, as above mentioned, at one of its wide parts, will show a bluish-black metallic mirror at the constriction beyond.

If quantitative determination is desired, the glass tube is heated in two places so as to cause all hydrogen arsenide to be decomposed. To collect, however, the arsenic from any gas that might escape, the end of the tube is inverted and placed into solution of nitrate of silver, which is decomposed by the hydrogen arsenide, silver and arsenous acid being formed. The arsenic solution should be introduced into the hydrogen generator in small portions, so as to produce not more hydrogen arsenide at a time than can be decomposed by the method given.

The only element which, under the same conditions, forms spots and mirrors similar to arsenic, is antimony; there are, however, sufficiently reliable tests to distinguish arsenic spots from those of antimony.

Arsenic spots treated with solution of hypochlorites (solution of bleaching-powder) dissolve readily; antimony spots are not affected. When nitric acid is added to an arsenic spot, evaporated to dryness and moistened with a drop of silver nitrate, it turns brick-red; antimony spots treated in like manner remain white. Arsenic spots dissolved in ammonium sulphide and evaporated to dryness show a bright yellow, antimony spots an orange-red residue.

Fig. 16.



Student's apparatus for making arsenic spots.

Fig 16 represents a simpler form of Marsh's apparatus, which generally will answer for students' tests.

Preparatory treatment of organic matter for arsenic analysis. If organic matter is to be examined for arsenic (or for any other metallic poison) it ought to be treated as follows: The substance, if not liquid, is cut into pieces, well mashed and mixed with water; the liquid or semi-liquid substance is heated in a porcelain dish over a steam bath with hydrochloric acid and potassium chlorate until the mass has a uniform light-yellow color and has no longer an odor of chlorine. By this operation all poisonous metals (lead and silver excepted, because insoluble silver chloride and possibly insoluble lead sulphate are formed) are rendered soluble even when present as sulphides, and may now be separated by filtration from some remaining solid matter. The clear solution is heated and treated with hydrosulphuric acid gas for several hours, when arsenic and all metals of the arsenic and lead groups are precipitated as sulphides, a little organic matter also being precipitated generally.

The precipitate is collected upon a small filter and treated with warm ammonium sulphide, which dissolves the sulphides of arsenic and antimony, leaving behind the sulphides of the lead group, which may be dissolved in nitric, or, if mercury be present, in nitro-hydrochloric acid, and the solution tested by the methods mentioned for the respective metals. The ammonium sulphide solution is evaporated to dryness, this residue mixed with nitrate and carbonate of sodium, and the mixture fused in a small porcelain crucible. By the oxidizing action of the nitrate, both sulphides are converted into the higher oxides, arsenic forming sodium arsenate, antimony forming antimonic oxide. By treating the mass with warm water, sodium arsenate is dissolved and may be filtered off, while antimonic oxide remains undissolved, and may be dissolved in hydrochloric acid. Both solutions may now be used for making the respective tests for arsenic or antimony.

Antidotes. Moist, recently prepared ferric hydroxide or dialyzed iron are the best antidotes, insoluble ferric arsenite or arsenate being formed. Vomiting should be induced by tickling the fauces or by administering zinc sulphate, but not tartar emetic.

QUESTIONS.—291. Which metals belong to the arsenic group? what are their characteristics? 292. Which non-metallic elements does arsenic resemble? Mention some of the compounds showing this analogy. 293. How is arsenic obtained in the metallic state; what are its physical and chemical properties; how does heat act upon it? 294. What is white arsenic? State its composition, mode of manufacture, appearance, solubility, and other properties. 295. Which three solutions, containing arsenic, are official, and what is their composition? 296. How is arsenic acid obtained from arsenous oxide, and which arsenate is official? 297. State composition and properties of arsenetted hydrogen, and explain its formation. What use is made of it in testing for arsenic? 298. State the composition of realgar, orpiment, Scheele's green, and Schweinfurth green. 299. Give a detailed description of the process by which arsenic can be detected in organic matter. 300. Describe in detail the principal tests for arsenic.

31. ANTIMONY—TIN—GOLD—PLATINUM—MOLYBDENUM.

Antimony, Sb = 119.6 (*Stibium*). This metal is found in nature chiefly as the trisulphide, Sb_2S_3, an ore which is known as *black antimony, crude antimony,* or *stibnite.*

The metal is obtained from the sulphide by roasting, when it is converted into oxide, which is reduced by charcoal. Antimony is a brittle, bluish-white metal, having a crystalline structure; it fuses at 450° C. (842° F.), and may at a higher temperature be distilled without change, provided air is excluded; heated in air it burns brilliantly.

Antimony is used in a number of important alloys, for instance, in type-metal, an alloy of lead, tin, and antimony.

Antimony trisulphide, Antimonii sulphidum, Sb_2S_3 = 335.2 (*Antimonous sulphide, Antimony sulphide*). The above-mentioned native sulphide, the black antimony, is found generally associated with other ores or minerals, from which it is freed by heating the masses, when the antimony sulphide fuses and is made to run off into suitable vessels for cooling. Thus obtained it forms steel-gray masses of a metallic lustre, and a striated, crystalline fracture, forming a grayish-black, lustreless powder, which is insoluble in water, but soluble in hydrochloric acid with liberation of hydrogen sulphide.

When finely powdered antimonous sulphide is treated with water of ammonia to remove any traces of arsenic (which is frequently found in this ore) and the washed sulphide dried, the *purified antimony sulphide* of the U. S. P. is obtained.

Antimonous sulphide found in nature is crystallized and *steel-gray* (Plate V., 6), but it may be obtained also in an amorphous condition as an *orange-red* (Plate V., 5) powder by passing hydrogen sulphide through an antimonous solution. By heating the orange-red sulphide, it is converted into the black variety.

Sulphurated antimony, Antimonium sulphuratum (*Oxysulphide of antimony, Kermes mineral*), chiefly antimony trisulphide with some antimony oxide. This preparation is made by boiling purified antimonous sulphide with solution of sodium hydroxide, and adding to the hot solution sulphuric acid as long as a precipitate is formed, which is collected and dried.

It is a reddish-brown amorphous powder, insoluble in water, soluble in hydrochloric acid or sodium hydroxide.

The sulphides and oxides of antimony, like those of arsenic, combine with many metallic sulphides or oxides to form sulpho-salts or oxy-salts. Thus the sodium sulph-antimonite, Na_3SbS_3, and the sodium antimonite, $NaSbO_2$, are formed when antimonous sulphide is boiled with sodium hydroxide.

$$Sb_2S_3 + 4NaOH = Na_3SbS_3 + NaSbO_2 + 2H_2O.$$

By the addition of sulphuric acid, both salts are decomposed, sodium sulphate is formed, and antimonous sulphide is precipitated:

$$Na_3SbS_3 + NaSbO_2 + 2H_2SO_4 = Sb_2S_3 + 2Na_2SO_4 + 2H_2O.$$

While the above is the principal reaction, there is formed also some antimony oxide.

Experiment 37. Boil about 2 grammes of finely powdered black antimony with a solution of 2 grammes of sodium hydroxide in 80 c.c. of water for about one hour, stirring frequently and occasionally adding water to preserve the same volume. Filter the warm liquid through paper or muslin and add dilute sulphuric acid so long as it produces a precipitate. Collect, wash, and dry the precipitated red powder, which is chiefly amorphous antimonous sulphide with oxide.

Antimony pentasulphide, Sb_2S_5 (*Golden sulphuret of antimony*). A red powder, which, like antimonous sulphide, forms sulpho-salts. It may be obtained by precipitation of acid solutions of antimonic acid by hydrosulphuric acid.

Antimonous chloride, $SbCl_3$ (*Antimony terchloride, Butter of antimony*). Obtained by boiling the native sulphide with hydrochloric acid:

$$Sb_2S_3 + 6HCl = 3H_2S + 2SbCl_3.$$

The clear solution is evaporated and the remaining chloride distilled, when it is obtained as a white, crystalline, semi-transparent mass.

By passing chlorine over antimonous chloride it is converted into *antimonic chloride*, $SbCl_5$, which is a fuming liquid.

Experiment 38. Boil about 2 grammes of black antimony with 10 c.c. of hydrochloric acid until most of the sulphide is dissolved. Set aside for subsidence, pour off the clear solution of antimonous chloride, evaporate to about half its volume and use solution for next experiment.

Antimonous oxide, Antimonii oxidum, $Sb_2O_3 = 287.2$ (*Antimony trioxide*). When antimonous chloride is added to water, decomposition takes place, and an oxychloride of antimony, $2SbCl_35Sb_2O_3$, is precipitated:

$$12SbCl_3 + 15H_2O = 2SbCl_3.5Sb_2O_3 + 30HCl.$$

This white precipitate was formerly known as *powder of Algaroth.*

It is completely converted into oxide by treating it with sodium carbonate:

$$2SbCl_3\,5Sb_2O_3 + 3Na_2CO_3 = 6Sb_2O_3 + 6NaCl + 3CO_2.$$

The precipitate when washed and dried is a heavy, grayish-white, tasteless powder, insoluble in water, soluble in hydrochloric acid, and also in a warm solution of tartaric acid. Antimonous oxide, while yet moist, dissolves readily in potassium acid tartrate, forming the *double tartrate of potassium and antimony*, or *tartar emetic*, which salt will be more fully considered hereafter.

Experiment 39. Pour the antimonous chloride solution (obtained by Experiment 38), which should have been boiled sufficiently to expel all hydrogen sulphide, into 100 c.c. of water, wash by decantation the white precipitate of oxychloride thus obtained, and add to it an aqueous solution of about 1 gramme of sodium carbonate. After effervescence ceases, collect the precipitate on a filter, wash well and treat some of the precipitate, while yet moist, with a solution of potassium acid tartrate, which dissolves it readily, forming tartar emetic. (For the latter compound see index.)

Antidotes. Poisonous doses of any preparation of antimony are generally quickly followed by vomiting: if this, however, have not occurred, the stomach-pump must be applied. Tannic acid in any form, or recently precipitated ferric hydroxide, should be administered.

Analytical reactions.

(A solution of antimonous chloride, $SbCl_3$, may be used.)

1. Add hydrogen sulphide to an acidified solution of antimony: an orange-red precipitate of antimonous or antimonic sulphide (Sb_2S_3 or Sb_2S_5) is produced (Plate V., 5).

2. Add ammonium sulphide to the precipitated sulphide of antimony: this is dissolved and may be re-precipitated by neutralizing with an acid.

3. Produce a concentrated solution of antimonous chloride by evaporation or by dissolving the sulphide in hydrochloric acid, and pour it into water: a white precipitate of oxychloride is formed. (See explanation above.)

4. Add sodium hydroxide, ammonium hydroxide, or sodium carbonate: in either case white antimonous hydroxide $Sb(OH_3)$ is produced, which is soluble in sodium hydroxide.

5. Boil a piece of metallic copper in the solution of antimonous chloride: a black deposit of antimony is formed upon the copper. By heating the latter in a narrow test-tube, the antimony is volatilized and deposited as a white incrustation of antimonous oxide upon the glass.

6. Use Gutzeit's or Marsh's test as described under analytical reactions for arsenic.

Tin, Sn = 118.8 (*Stannum*). This metal is found in nature chiefly as stannic oxide or *tin-stone*, SnO_2, from which the metal is easily obtained by heating with coal:

$$SnO_2 + 2C = Sn + 2CO.$$

Tin is an almost silver-white, very malleable metal, fusing at the comparatively low temperature of 228° C. (440° F.). It is used in many alloys, in the silvering of looking-glasses by tin-amalgam, and chiefly in the manufacture of tin-plate, which is sheet-iron covered with a thin layer of tin.

Tin is bivalent in some compounds, quadrivalent in others. These combinations are distinguished as stannous and stannic compounds.

Stannous chloride, $SnCl_2$ (*Protochloride of tin*). Obtained by dissolving tin in hydrochloric acid by the aid of heat:

$$Sn + 2HCl = SnCl_2 + 2H.$$

Sufficiently evaporated, the solution yields crystals of the composition $SnCl_2.2H_2O$. Stannous chloride is a strong deoxidizing agent, frequently used as a reagent for arsenic, mercury, and gold, which metals are precipitated from their solutions in the metallic state. It is used also in calico printing.

Stannic chloride, $SnCl_4$ (*Perchloride of tin*). Stannous chloride may be converted into stannic chloride either by passing chlorine through its solution or by heating with hydrochloric and nitric acids.

Analytical reactions.

(Stannous chloride, $SnCl_2$, and stannic chloride, $SnCl_4$, may be used.)

1. Add hydrogen sulphide to solution of a stannous salt: brown stannous sulphide is precipitated (Plate V., 7):

$$SnCl_2 + H_2S = 2HCl + SnS.$$

The precipitate is soluble in ammonium sulphide.

2. Add hydrosulphuric acid to a solution of a stannic salt: yellow stannic sulphide is precipitated (Plate V., 8):

$$SnCl_2 + 2H_2S = 4HCl + SnS_2.$$

The precipitate is soluble in ammonium sulphide.

3. Sodium or potassium hydroxide added to a stannous salt, produces a white precipitate of stannous hydroxide, $Sn(OH)_2$. The same

reagents added to a stannic salt produce white stannic acid, H_2SnO_3. Both precipitates are soluble in excess of the alkali.

Gold, Au = 196.7 (*Aurum*). Gold occurs in nature chiefly in the free state, often associated with silver, copper, and possibly with other metals. This impure gold is separated from most of the adhering sand and rock by a mechanical process of washing, in which advantage is taken of the high specific gravity of the metallic masses. The remaining mixture of heavy material is treated with mercury, which dissolves gold and silver, leaving behind most other impurities. The gold amalgam is placed in a retort and heated, when the mercury distils over, while the gold is left behind. If this should contain silver, the metals may be separated by treating the alloy with hot sulphuric acid, which dissolves silver, leaving gold behind.

Pure gold is too soft for general use, and therefore is alloyed with various proportions of silver and copper. American coin is an alloy of 90 parts of gold and 10 parts of copper; jeweller's gold contains generally 75 per cent. (18 carat) of gold, the other 25 per cent. being copper and silver; the varying proportions are well indicated by the color.

Gold is not affected by either hydrochloric, nitric, or sulphuric acid, but is dissolved by nitro-hydrochloric acid, by free chlorine or bromine, and by mercury, with which it forms an amalgam.

Gold is trivalent generally, as in auric chloride, $AuCl_3$, but most likely also univalent in some compounds, as in aurous chloride, AuCl.

Auric chloride, $AuCl_3$ (*Gold chloride*). Obtained by dissolving pure gold in nitro-hydrochloric acid and evaporating the solution to dryness. A mixture of equal parts of auric chloride and sodium chloride is official under the name of *gold and sodium chloride*. It is an orange-yellow, very soluble powder.

Analytical reactions.

(Auric chloride, $AuCl_3$, may be used.)

1. Add hydrogen sulphide to solution of gold: brown auric sulphide, Au_2S_3, is precipitated, which is soluble in yellow ammonium sulphide.

2. Add ferrous sulphate to solution of gold and set aside for a few hours: metallic gold is precipitated as a dark powder, which by fusion is converted into a metallic mass.

3. Many other reagents cause the separation of metallic gold from its solution, as, for instance, oxalic acid, sulphurous and arsenous acids, potassium nitrite, etc.

Platinum, Pt = 194.3. Platinum, like gold, is found in nature in the free state, the chief supply being derived from the Ural mountains, where it is found associated with a number of metals (iridium, ruthenium, osmium, palladium, rhodium) resembling platinum in their properties.

Platinum is of great importance and value on account of its high fusing-point and its resistance to the action of most chemical agents, for which reason it is used in the manufacture of vessels serving in chemical operations.

Platinum, when dissolved in nitro-hydrochloric acid, forms platinic chloride, $PtCl_4$, a salt frequently used as a reagent for potassium or ammonium salts, with which it forms insoluble double chlorides of the composition $PtCl_4.(KCl)_2$ and $PtCl_4.(NH_4Cl)_2$. By heating the latter salt sufficiently it is decomposed and metallic platinum is left as a gray spongy mass.

Molybdenum, Mo = 95.9. This metal is found in nature chiefly as sulphide, MoS_2, from which, by roasting, molybdic oxide, MoO_3, is obtained. The oxide, when dissolved in water, forms an acid which combines with metals, forming a series of salts termed molybdates. Of interest is *ammonium molybdate,* a solution of which in nitric acid is an excellent reagent for phosphoric acid, with which it forms a yellow precipitate, insoluble in acids, soluble in ammonium hydroxide.

QUESTIONS.—301. How is antimony found in nature, and what are the properties of this metal? 302. State the composition of antimonous sulphide, and its color when crystallized and amorphous. 303. How do hydrochloric acid and alkali hydroxides act upon antimonous sulphide? 304. What is the sulphurated antimony of the U. S. P.? 305. Mention the two chlorides of antimony and state their properties. 306. How is antimonous oxide made, and what is it used for? 307. Give tests for antimony. 308. State the use made of tin in the metallic state; mention the two chlorides of tin, and what stannous chloride is used for. 309. How are gold and platinum found in nature; by what acid may they be dissolved, and what is the composition of the compounds formed? 310. Which is the most important compound of molybdenum, and what is it used for?

Summary of analytical characters of metals of the arsenic group.

	Arsenic.	*Antimony.*	*Tin.*	*Gold.*	*Platinum.*
Hydrogen sulphide .	Yellow precipitate.	Orange precipitate	Yellow or brown precipitate.	Black precipitate	Dark-brown precipitate.
Precipitate heated in strong hydrochloric acid . .	Insoluble.	Soluble.	Soluble.	Insoluble.	Insoluble.
Potassium hydroxide	....	White precipitate	White precipitate.	Brownish precipitate, soluble in excess.	With excess of hydrochloric acid a yellow precipitate.
Ammonia water . .	....	White precipitate.	White precipitate.	Brownish yellow precipitate.	
Gutzeit's test . . .	Yellow stain, turning dark with water.	Dark stain.	....	....	....
Fleitmann's test . .	Dark stain.	....	....	....	....

V.

ANALYTICAL CHEMISTRY.

32. INTRODUCTORY REMARKS AND PRELIMINARY EXAMINATION.

General remarks. Analytical chemistry is that part of chemistry which treats of the different analytical methods by which substances are recognized and their chemical composition determined. This determination may be either qualitative or quantitative, and, accordingly, a distinction is made between a *qualitative analysis*, by which simply the nature of the elements (or groups of elements) present in the substance under examination is determined, and a *quantitative analysis*, by which also the exact amount of these elements is ascertained.

In this book qualitative analysis will be considered chiefly, as the methods for quantitative determinations of the different elements are so numerous and so varied that a detailed description of them would occupy more space than can be devoted to analytical chemistry in this work. Some brief directions concerning quantitative determinations, especially by volumetric methods, are given in Chapter 36. Everyone studying analytical chemistry should do it practically, that is, should perform for himself in a laboratory all those reactions which have been mentioned heretofore as characteristic of the different elements and their compounds, and, furthermore, should make himself acquainted with the methods by which substances are recognized when mixed with others, by analyzing various complex substances.

Such a course of practical work in a suitable laboratory is of the greatest advantage to all studying chemistry, and students cannot be too strongly advised to avail themselves of any facilities offered in performing chemical experiments, analytically or otherwise.

Apparatus needed for qualitative analysis.

1. Iron stand. (Fig. 17.)
2. Bunsen lamp with flexible tube (Fig. 17), or (where without gas-supply) spirit-lamp and alcohol.

3. Test-tube stand and one dozen assorted test-tubes. (Fig. 18.)
4. Three small beakers from 100 to 150 c.c. capacity. (Fig. 19, A.)
5. Two flasks of 100 to 150 c.c. capacity. (Fig. 19, B.)

Fig. 17.

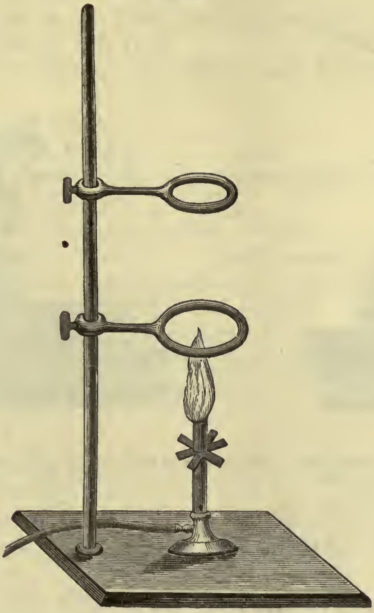


Fig. 18.

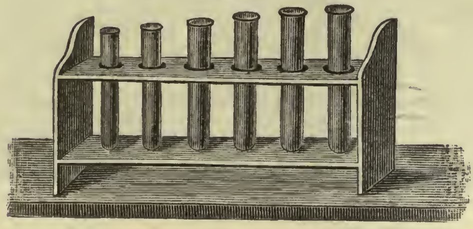
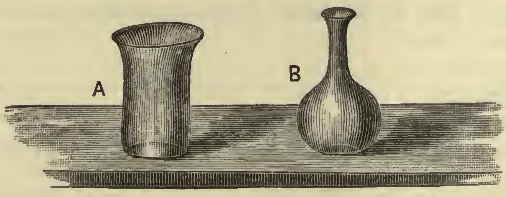


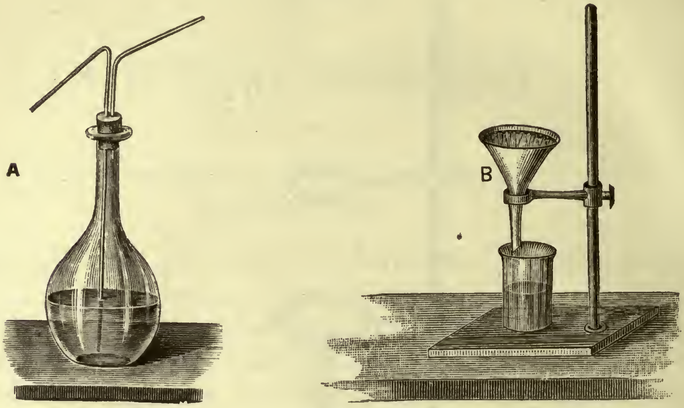
Fig. 19.



6. Wash-bottle of about 400 c.c. capacity. (Fig. 20, A.)
7. Three small glass funnels, about one and a half to two inches in diameter. (Fig. 20, B.)

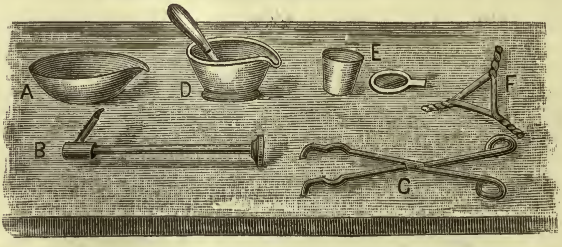
8. A few pieces of glass tubing about ten inches long, and some India-rubber tubing to fit the glass tubing.
9. Three glass rods.

FIG. 20.



10. Three small porcelain evaporating dishes, about two inches in diameter (Fig. 21, A.)
11. Blowpipe. (Fig. 21, B.)
12. Crucible tongs. (Fig. 21, C.)

FIG. 21.



13. Round and triangular file
14. Wire gauze, about six inches square, or sand tray.
15. One square inch of platinum foil (not too light), and six inches of platinum wire.
16. Filter-paper.
17. Pair of scissors.
18. One or two dozen assorted corks.
19. Sponge and towel.
20. Two watch-glasses.
21. Small pestle and mortar. (Fig. 21, D.)
22. Small porcelain crucible.
23. Small platinum crucible. (Fig. 21, E.)
24. Wire triangle to support the crucible. (Fig. 21, F.)

Reagents needed in qualitative analysis.

a. Liquids.

1. Sulphuric acid, sp. gr. 1.84, H_2SO_4.
2. Sulphuric acid diluted, sp. gr 1.068 (1 part sulphuric acid, 9 parts water).
3. Hydrochloric acid, sp gr. 1.16, HCl.
4. Hydrochloric acid diluted, sp. gr. 1.049 (6 parts hydrochloric acid, 13 parts water).
5. Nitric acid, sp. gr. 1.42, HNO_3.
6. Acetic acid, sp. gr 1 048, $C_2H_4O_2$.
7. Hydrogen sulphide, either the gas or its solution in water, H_2S.
8. Ammonium sulphide, $(NH_4)_2S$.
9. Ammonium hydroxide (water of ammonia), NH_4OH.
10. Ammonium carbonate, $(NH_4)_2CO_3$ A solution of one part of the commercial salt in a mixture of four parts of water and one part of water of ammonia.
11. Ammonium chloride, NH_4Cl; ten per cent solution.
12 Ammonium oxalate, $(NH_4)_2C_2O_4$; five per cent. solution.
13. Ammonium molybdate, $(NH_4)_2MoO_4$. A five per cent. solution of the salt in a mixture of equal parts of water and nitric acid.

14. Sodium hydroxide, $NaOH$.	Ten per cent. solutions.
15. Sodium carbonate, Na_2CO_3.	
16. Sodium phosphate, Na_2HPO_4.	
17. Sodium acetate, $NaC_2H_3O_2$.	
18. Potassium chromate, K_2CrO_4.	
19. Potassium dichromate, $K_2Cr_2O_7$.	
20. Potassium iodide, KI.	Five per cent. solutions.
21. Potassium ferrocyanide, $K_4Fe(CN)_6$.	
22. Potassium ferricyanide, $K_6Fe_2(CN)_{12}$.	
23 Potassium sulphocyanate, $KCNS$.	
24. Magnesium sulphate, $MgSO_4$.	Ten per cent. solutions.
25. Barium chloride, $BaCl_2$.	
26. Calcium chloride, $CaCl_2$.	
27. Calcium hydroxide, $Ca(OH)_2$ (lime-water).	Saturated solutions.
28. Calcium sulphate, $CaSO_4$.	
29. Ferric chloride, Fe_2Cl_6.	Five per cent. solutions.
30. Lead acetate, $Pb.(C_2H_3O_2)_2$.	
31. Silver nitrate, $AgNO_3$.	
32. Mercuric chloride, $HgCl_2$.	
33. Platinic chloride, $PtCl_4$.	

34. Stannous chloride, $SnCl_2.2H_2O$; ten per cent. solution.
35. Solution of indigo
36. Alcohol, C_2H_5OH
37. Sodium cobaltic nitrite solution, $Co_2(NO_2)_6.6NaNO_2 + H_2O$. Four grammes of cobaltous nitrate, $Co(NO_3)_2$ $6H_2O$, and 10 grammes of sodium nitrite, $NaNO_2$, are dissolved in about 50 c.c. of water, 2 c.c. of acetic acid are added, and then water to make 100 c c.
38. Alkaline mercuric-potassium iodide solution (Nessler's solution). Five grammes of potassium iodide are dissolved in hot water, and to this is added a hot solution, made by dissolving 2.5 grammes of mercuric chloride in 10 c.c. of water. To the turbid red mixture is added a solution made by dissolving 16

grammes of potassium hydroxide in 40 c.c. of water, and the whole diluted to 100 c.c. Some mercuric iodide deposits on cooling, and may be left in the bottle, the clear solution being decanted as needed.

b. Solids.

1. Litmus or blue and red litmus paper.
2. Turmeric paper.
3. Sodium carbonate, dried, Na_2CO_3.
4. Sodium biborate, borax, $Na_2Bo_4O_7.10H_2O$.
5. Sodium-ammonium-hydrogen phosphate (microcosmic salt), $Na(NH_4)HPO_4.4H_2O$.
6. Potassium carbonate, K_2CO_3.
7. Potassium nitrate, KNO_3.
8. Potassium chlorate, $KClO_3$.
9. Potassium permanganate, $KMnO_4$.
10. Potassium cyanide, KCN.
11. Calcium hydroxide, $Ca(OH)_2$.
12. Ferrous sulphide, FeS.
13. Ferrous sulphate, $FeSO_4.7H_2O$.
14. Manganese dioxide, MnO_2.
15. Zinc, granulated, Zn.
16. Copper, Cu
17. Cupric oxide, CuO
18. Cupric sulphate, $CuSO_4.5H_2O$.
19. Tartaric acid, $H_2C_4H_4O_6$.
20. Tannic acid, $H.C_{14}H_9O_9$
21. Pyrogallic acid, $C_6H_3(OH)_3$.
22. Diphenylamine, $(C_6H_5)_2NH$.
23. Starch, $C_6H_{10}O_5$.

While the apparatus and reagents here enumerated are the more important ones, the analyst will occasionally require others not mentioned in the above list.

General mode of proceeding in qualitative analysis. Every step taken in analysis should be properly written down in a note-book, and these remarks should be made *directly after a reaction has been performed*, and not after the nature of the substance has been revealed by perhaps numerous reactions.

Not only the reactions by which *positive* results have been obtained should be noted, but also those tests and reagents mentioned which have been applied with *negative* results—that is, which have been applied without revealing the presence of any substance, or any group of substances. Such negative results are, however, positive in so far as they prove the absence of a certain substance, or certain substances, for which reason they are of direct value, and should be noted.

In comparing, finally, the result obtained by the analysis with the notes taken during the examination, none of them should be contradictory to the conclusions drawn. If, for instance, the preliminary examination showed the substance to have been volatilized by heating upon platinum foil *with the exception of a very slight residue*, and if, afterward, other tests show the presence of ammonia and hydrochloric acid and the absence of everything else, and if, then, the conclusion be drawn that the substance is *pure* ammonium chloride, this conclusion must be incorrect, because pure ammonium chloride is wholly volatile, and does not leave a residue. It will then be the task of the operator to find where the mistake occurred, and to correct it.

Use of reagents. A mistake made by most beginners in analyzing is the use of too large quantities both of the substance applied for testing and of the reagents added. This excessive use of material is not only a waste of money, but, what is of greater importance, a waste of time. Some experience in analyzing will soon convince the student of the truth contained in this remark, and will also enable him to select the correct quantities of materials to be used, which rarely exceed 0.2–1.0 gramme. A smaller amount frequently may answer, and a much larger quantity may occasionally be needed, as, for instance, in cases where highly diluted reagents, such as calcium sulphate solution, lime-water, hydrogen sulphide water, etc., are applied.

Preliminary examination. This examination includes the following points:

1. **Physical properties.** Solid or liquid; crystallized or amorphous; color, odor, hardness, gravity, etc. (On account of possible poisonous properties, the greatest care should be exercised in tasting a substance.)

2. **Action on litmus.** Examined by holding litmus-paper in the liquid, or by placing the powdered solid upon red and blue litmus-paper, moistened with water. (It should be remembered that many normal salts, as, for instance, aluminum sulphate, ferrous sulphate, etc., have an acid reaction to litmus-paper, and that such a reaction consequently is not conclusive of the presence of a free acid, nor even of an acid salt.)

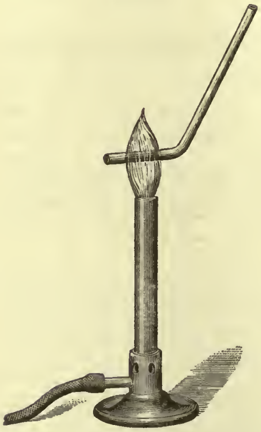
3. **Heating on platinum foil or in a dry glass tube, open at both ends.** (If the substance to be examined be a liquid, it should

be evaporated in a small porcelain dish to see whether a solid residue be left or not. If a residue be left, it should be treated like a solid.) The heating of a small quantity of a solid substance upon platinum foil held over the flame of a Bunsen burner or of an alcohol lamp, is a test which should *never* be omitted, as it discloses in most cases the fact whether the substance is of an organic or inorganic nature. Most organic (non-volatile) substances, when thus heated, will burn with a luminous flame, leaving in many cases a black residue of carbon, which, upon further heating, disappears. In cases where the organic nature of a compound is not clearly demonstrated by heating on platinum foil, the substance is heated with an excess of cupric oxide in a test-tube or other glass tube, provided with a delivery-tube, which passes into lime-water. Upon heating the mixture, the carbon of the organic matter is converted into carbon dioxide, which renders lime-water turbid.

The analytical processes by which the nature of an organic substance is determined, are not considered in this part of the book, but will be mentioned when considering the carbon compounds.

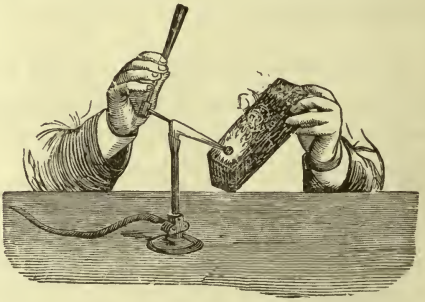
An inorganic substance, heated on platinum foil, may either be volatilized, fused, change color, become oxidized, suffer decomposition, or remain unchanged. (See Table I., page 232.)

FIG. 22.



Heating of solids in bent glass tube.

FIG. 23.



Heating on charcoal by means of blowpipe.

Some substances, containing small quantities of water enclosed between the crystals (common salt, for instance), *decrepitate* when heated, the small fragments being thrown from the foil; such substances should be heated in a dry test-tube to expel the water and then be examined on platinum foil.

In many cases it is preferable to heat the substance in a bent glass tube, as shown in Fig. 22, instead of on platinum foil, because volatile products evolved during the process of heating may become recondensed in the cooler part of the tube, and thus saved for further examination.

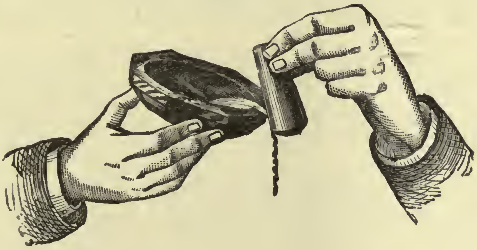
The presence of water, sulphur, mercury, arsenic, etc., may often be readily demonstrated by this mode of operating.

4. Heating on charcoal by means of the blowpipe. This test reveals the presence of chlorates and nitrates by the vivid combustion of the charcoal (known as *deflagration*), which takes place in consequence of the oxidizing action of these substances.

Arsenic is indicated by a characteristic odor of garlic.

5. Heating on charcoal with sodium carbonate and potassium cyanide. A small quantity of the finely powdered substance is mixed with twice its weight of potassium cyanide and dry sodium carbonate. This mixture is placed in a small hole made in a piece of charcoal, and heat applied by means of the blowpipe (see Fig. 23). Many metallic compounds may be recognized by this test, the metals being liberated and found as metallic globules or shining particles in the fused mass after this has been removed from the charcoal and washed with water in a small mortar. (See Fig. 24.)

FIG. 24.

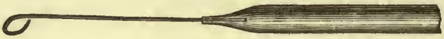


A characteristic incrustation is formed by some metals, due to the precipitation of a metallic oxide around the heated spot on the charcoal.

If sulphur as such, or in any form of combination, be present in the substance examined by this test, the fused mass contains a sulphide of the alkali (*hepar*), which may be recognized by placing it on a piece of bright silver (coin) moistened with a drop of water, when the silver will be stained black in consequence of the formation of silver sulphide. The presence of the alkali sulphide may also be demonstrated by the addition of a few drops of hydrochloric acid to the fused mass, when hydrogen sulphide is evolved and may be recognized by its odor.

6. Flame tests. Many substances impart a characteristic color to a non-luminous flame. The best mode of performing this test is as follows: A platinum wire is cleaned by washing in hydrochloric acid and water, and heating it in the flame until the latter is no longer colored. One end of the wire is fused in a short piece of glass tubing (see Fig. 25), the other end is bent so as to form a small loop, which is heated, dipped into the substance to be examined, and again held in the lower part of the flame, which then becomes colored.

FIG. 25.



Some substances show the color-test after being moistened with hydrochloric or sulphuric acid.

A second method of showing flame reactions is to mix the substance with alcohol in a small dish; the alcohol, upon being ignited, shows a colored flame, especially in the dark.

7. Colored borax beads. The compounds of some metals when fused with glass, impart to it characteristic colors. For analytical purposes not the silica-glass, but borax-glass is generally used. This latter is made by dipping the loop of a platinum wire in powdered borax and heating it in the flame (directly, or by means of the blowpipe) until all water has been expelled and a colorless, transparent bead has been formed. To this colorless bead a little of the finely powdered substance is added and the bead strongly heated. The metallic compound is chemically acted upon by the boric acid, a borate being formed which colors the bead more or less intensely, according to the quantity of the metallic compound used.

Some metals (copper, for instance) forming two series of compounds, give different colors to the bead when present in either the higher or lower state of oxidation.

By modifying the blowpipe flame so as either to oxidize (by supplying an excess of atmospheric oxygen) or deoxidize (by allowing some unburnt carbon to remain in the flame), the metallic compound in the bead may be made to assume the higher or lower state of oxidation. A copper bead may thus be changed from blue to red or red to blue, the blue bead containing the copper in the cupric, the red bead in the cuprous form. In some cases *microcosmic salt*, $NaNH_4HPO_4$, is used for making the bead.

8. Liquefaction of solid substances. Most solid substances have to be dissolved for analysis. The solution obtained may be either a simple or chemical solution. In a *simple solution* the dissolved body retains all of its original properties, with the exception of its shape, and may be re-obtained by evaporation. Sodium chloride and sugar dissolved in water form simple solutions. A *chemical solution* is one in which the chemical composition of the substance has been changed during the process of dissolving, as, for instance when calcium carbonate is dissolved in hydrochloric acid; this solution now contains and leaves on evaporation calcium chloride. The solvents used are water, or the mineral acids for substances insoluble in water, especially dilute, or, if necessary, strong hydrochloric acid. The dissolving action of the acid should be facilitated by the aid of heat. Nitric or even nitro-hydrochloric acid may have to be used in some cases.

Three mistakes are frequently made by beginners in dissolving substances in acids, viz.: The substance is not powdered as finely as it should be; sufficient time is not given for the acid to act; too large an excess of the acid is used.

If a substance is partly dissolved by water and partly by one or more other solvents, it may be well to examine the different solutions separately.

Substances insoluble in water and in acids have to be rendered soluble by fusion with a mixture of potassium and sodium carbonate, or with potassium acid sulphate, or by the action of hydrofluoric acid.

The insoluble sulphates of the alkaline earths, when fused with the alkaline carbonates, are converted into carbonates, while the sulphates of the alkalies are formed. The latter compounds may be eliminated by washing the fused mass with water and filtering: the solid residue upon the filter contains the carbonates of the alkaline earths, which may be dissolved in hydrochloric acid.

Insoluble silicates may be decomposed by the methods mentioned on page 98.

QUESTIONS.—311. What is analytical chemistry, and what is the object of qualitative and of quantitative analysis? 212. What properties of a substance

TABLE I.—Preliminary examination.

Heat the solid substance upon platinum foil, or in a dry, narrow glass tube open at both ends.	*Combustible* are: All **organic compounds, carbon, sulphur, phosphorus,** etc. *Easily volatilized* are: All compounds of **ammonium** and **mercury**, most of **arsenic**, some of **antimony**, etc. (Heat in a glass tube as directed on page 227.) *Fusible* are: Most of the salts of the **alkalies**, and some of those of the **alkaline earths**, many metals, etc. *Infusible* are: Salts of the **earths**, and most salts of the **alkaline earths** and **heavy metals**, most **silicates**, etc. *Assume a darker color:* Many **oxides of the heavy metals** and **their salts** (oxides of zinc, antimony, lead, etc.). *Evolve water:* Many **salts containing water of crystallization**, some **hydroxides**, etc. *Decrepitate:* Some **salts**, sodium chloride, for instance.
Heat the solid substance on charcoal.	*Deflagrate:* **Nitrates, chlorates, iodates, bromates**, etc. Give *garlic odor:* Most compounds of **arsenic.**
Heat the substance, mixed with sodium carbonate and patassium cyanide, on charcoal.	Give *hepar:* **Sulphur** and all **its compounds.** Give *bright metallic grains without incrustation:* Compounds of **gold, silver, copper, tin.** Give *bright metallic grains with incrustation:* Compounds of **lead, bismuth, antimony.** Give *gray infusible powder:* Compounds of **iron, cobalt, nickel, platinum.**
Heat the substance on platinum wire in a non luminous flame.	*Yellow* flame, compounds of **sodium.** *Violet* flame, compounds of **potassium.** *Crimson* flame, compounds of **lithium** or **strontium.** *Orange* flame, compounds of **calcium** *Yellowish-green* flame, compounds of **barium** or **molybdenum.** *Green* flame, compounds of **copper, phosphoric** or **boric acids.** *Blue* flame, compounds of **arsenic, antimony, lead,** or **cupric chloride.**
Heat a colorless borax bead with very little of the substance.	*Green* bead, compounds of **chromium.** *Blue* bead, compounds of **cobalt** or **copper** in the oxidizing flame. *Red* bead, compounds of **copper** in the reducing flame. *Violet* bead, compounds of **manganese.** *Yellow* to *brown* bead, compounds of **iron.** *Colorless* bead, compounds of the **light metals** and those of the **arsenic group**; also **silver, bismuth, lead,** etc.

33. SEPARATION OF METALS INTO DIFFERENT GROUPS.

General remarks. The preliminary examination will, in most cases, decide whether or not a metal or metals are present in the substance to be examined. If there be metals, the solution should be treated according to Table II., page 236, in order to find the group or groups to which these metals belong, and also to separate them into these groups, the individual nature of the metals themselves being afterward demonstrated by special methods.

The simplest method of separating from each other the 55 metals known, if all were in one solution, would be to add successively 55 different reagents, each of which should form an insoluble compound with but *one* of the metals. By separating this insoluble compound from the metals remaining in solution (by filtration), and by thus precipitating one metal after the other, they all could be easily separated. We have, however, no such 55 reagents, and are, consequently, compelled to precipitate a number of metals together, and the reagents used for this purpose are known as *group-reagents*.

They are:

1. *Hydrogen sulphide,* added to the solution previously acidified by hydrochloric acid. Precipitated are: the metals of the arsenic and lead groups as sulphides.
2. *Ammonium sulphide,* added after supersaturating with *ammonium hydroxide.* Precipitated are: the metals of the iron group and of the earths as sulphides or hydroxides.
3. *Ammonium carbonate.* Precipitated are: the metals of the alkaline earths as carbonates.
4. *In solution are left:* the metals of the alkalies and magnesium.

The order in which these group-reagents are added cannot be

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should be noticed first in making a qualitative analysis? 313. By what tests may organic compounds be distinguished from inorganic compounds? 314. Explain the terms decrepitation and deflagration. 315. Mention some substances which are completely volatilized by heat, some which are fusible, and some which are not changed by heating them. 316. What is meant by "hepar," and which element is indicated by the formation of hepar? 317. Mention some metals which may be liberated from their compounds by heating on charcoal with potassium cyanide and carbonate. 318. Which metallic compounds and which acids are capable of coloring a non-luminous flame? Name the colors imparted. 319. State the metals which impart characteristic colors to a borax bead. 320. Which solvents are used for liquefying solids, and what precautions should be observed in this operation?

reversed or changed, because ammonium sulphide added first would precipitate not only the metals of the iron group and the earths, but also the metals of the lead group; ammonium carbonate would precipitate also most of the heavy metals.

For the same reasons, in separating metals of the different groups, the group-reagents must be added in *excess*, that is, enough of them must be added to precipitate the total quantity of the metals of one group, before it is possible to test for metals of the next group. Suppose, for instance, a solution to contain a salt of bismuth only. Upon the addition of hydrogen sulphide to the acidified solution, a dark-brown precipitate (of bismuth sulphide) is produced, indicating the presence of a metal of the lead group. Suppose, further, that hydrogen sulphide has not been added in sufficient quantity to precipitate the whole of the bismuth, then ammonium sulphide, as the next group-reagent, would produce a further precipitation in the filtrate, which fact would lead to the assumption that a metal of the iron group was present, which, however, would not be the case.

If the solution contain but one metal, the group-reagents are added successively in small quantities to the same solution, until the reagent is found which causes a precipitation, which reagent is then added in somewhat larger quantity in order to produce a sufficient amount of the precipitate for further examination.

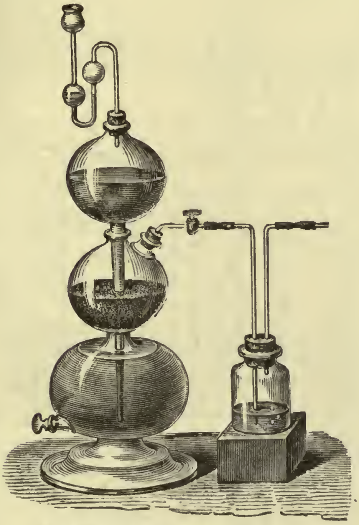
Acidifying the solution. Hydrosulphuric acid has to be added to the *acidified* solution for two reasons, viz.: In a neutral or alkaline solution some metals of the arsenic group (which are to be precipitated) would not be precipitated by hydrogen sulphide; some of the metals of the iron group (which are not to be precipitated) would be thrown down.

The best acid to be used in acidifying is dilute hydrochloric acid; but this acid forms insoluble compounds with a few of the metals of the lead group, causing them to be precipitated. Completely precipitated by hydrochloric acid are mercurous and silver compounds; partially precipitated are compounds of lead, chloride of lead being somewhat soluble in water. The precipitate formed by hydrochloric acid may be examined by Table III., page 238.

Hydrochloric acid added to a solution may, in a few cases (other than those just mentioned), cause a precipitate, as, for instance, when added to solutions containing certain compounds of antimony or bismuth (the precipitated oxychlorides of these metals are soluble in excess of the acid), to metallic oxides or hydroxides which have been dissolved by alkali hydroxides (for instance, hydroxide of zinc dissolved in potassium or ammonium hydroxide), to solutions of alkali silicates, when silica separates, etc.

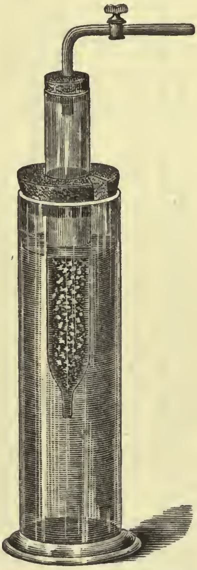
Addition of hydrogen sulphide. This reagent is employed either in the gaseous state (by passing it through the heated solution) or as hydrogen sulphide water. The latter reagent answers in those cases where but one metal is present; if, however, metals of the arsenic and lead groups are to be separated from metals of other groups, the gas must be used.

FIG. 26.



Apparatus for generating hydrogen sulphide.

FIG. 27.



Apparatus for generating hydrogen sulphide.

For generating hydrogen sulphide the directions given on page 107 may be followed. In place of the apparatus there mentioned for generating the gas, others may be used which have the advantage to the analyst that the supply of gas may be better regulated. Fig. 26 shows such an apparatus for the continuous preparation of the gas. It consists of three glass bulbs; the upper bulb, prolonged by a tube reaching to the bottom of the lowest one, is ground air-tight into the neck of the second. Ferrous sulphide is introduced into the middle bulb through the tubulure, which is then closed by a perforated cork through which connection is made with the wash-bottle. Acid poured in through the safety tube, runs into the bottom globe and rises to the ferrous sulphide in the second bulb. Upon closing the delivery tube, the pressure of the generated gas forces the liquid from the second bulb through the lower to the upper, thus preventing contact of acid and ferrous sulphide until the gas is used again.

A convenient and cheaper apparatus is shown in Fig. 27. A glass tube, drawn at its lower end to a small point and partly filled with pieces of ferrous sulphide, is suspended through a cork (not air-tight) in a cylinder containing the acid. The gas supply is regulated by closing or opening the stop-cock, and also by raising or lowering the tube in the acid.

TABLE II.—Separation of metals into different groups.

Add the following reagents successively to the same solution. Every time a precipitate is formed an excess of the precipitant is to be used; the precipitate is collected upon a filter, well washed, and treated by the tables mentioned. To the clear filtrate the next group-reagent is added. If the solution contains but one metal, generally it is sufficient to find by means of this table the group to which it belongs, and then to use the original solution for testing according to Tables III.–VIII.

Dilute hydrochloric acid precipitates:	**Hydrogen sulphide** precipitates:		**Ammonium hydroxide** and **sulphide** precipitate:	**Ammonium carbonate** precipitates:	**In solution** are left:
Metals of the **lead group.**		**Arsenic group.**	**Iron group** and **earths.**	**Alkaline earths.**	**Alkalies** and **magnesium.**
	Insoluble in ammonium sulphide.	Soluble in ammonium sulphide.			
Silver chloride, **Mercurous** chloride, **Lead** chloride, White. A precipitate may be caused by other substances than those mentioned. See page 234.	**Lead** sulphide, **Mercuric** sulphide, **Bismuth** sul phide, **Cupric** sulphide, Black. **Cadmium** sulphide, yellow.	**Arsenous** sulphide, yellow. **Antimonous** sulphide, orange. **Stannous** sulphide, brown. **Stannic** sulphide, yellow. **Auric** sulphide, brown. **Platinic** sulphide, brown.	**Ferrous** sulphide, black. **Cobaltous** sulphide, black. **Nickelous** sulphide, black. **Manganous** sulphide, flesh-colored. **Zinc** sulphide, white, **Chromic** hydroxide, green **Aluminum** hydroxide, white. A precipitate may be caused by other substances than those mentioned. See page 237.	**Calcium** carbonate, **Barium** carbonate, **Strontium** carbonate, White.	**Magnesium.** **Potassium.** **Sodium.** **Lithium.** **Ammonium.**
See Table III.	See Table IV.	See Table V.	See Table VI.	See Table VII.	See Table VIII.

In some cases sulphur is precipitated on the addition of hydrogen sulphide, while a change in color may take place. This change is due to the deoxidizing action of hydrogen sulphide, the hydrogen of this reagent becoming oxidized and converted into water, while sulphur is liberated. Thus, brown ferric compounds are converted into pale-green ferrous compounds; red solutions of acid chromates become green; and red permanganates or green manganates are decolorized.

The same deoxidizing action of hydrogen sulphide is the reason why this reagent cannot be employed in a solution containing free nitric acid, which latter compound oxidizes the hydrogen sulphide.

Separation of the metals of the arsenic from those of the lead group. The precipitate produced by hydrogen sulphide in acid solution contains the metals of the arsenic and lead groups. They are separated by means of ammonium sulphide, which dissolves the sulphides of the arsenic group, but does not act on those of the lead group.

Addition of ammonium sulphide. This reagent should never be added to the acid solution, but the solution should be previously supersaturated by ammonium hydroxide, as, otherwise, a precipitate of sulphur may be formed. The yellow ammonium sulphide is almost invariably a polysulphide of ammonium, that is, ammonium sulphide which has combined with one or more atoms of sulphur. If an acid be added to this compound, an ammonium salt is formed, hydrogen sulphide is liberated, and sulphur precipitated:

$$(NH_4)_2S_2 + 2HCl = 2NH_4Cl + H_2S + S.$$

Ammonium sulphide precipitates the metals of the iron group as sulphides, with the exception of chromium, which is precipitated as hydroxide; aluminum is precipitated in the same form of combination.

Ammonium sulphide (or ammonium hydroxide) causes also the precipitation of metallic salts which have been dissolved in acids, as, for instance, of the phosphates, borates, silicates, or oxalates of the alkaline earths, magnesium, and others. The processes by which the nature of some of these precipitates is to be recognized are found in Table VI., page 240.

Addition of ammonium carbonate. The reagent used is the commercial salt, dissolved in water, to which some ammonia water has been added. Heating facilitates complete precipitation of the carbonates of the alkaline earths.

34. SEPARATION OF THE METALS OF EACH GROUP.

TABLE III.—Treatment of the precipitate formed by hydrochloric acid.

<table>
<tr><td colspan="3">The precipitate may contain **silver, mercurous,** and **lead chlorides.** Boil the washed precipitate with much water, and filter while hot.</td></tr>
<tr><td rowspan="2">Filtrate may contain **lead chloride.** Add dilute sulphuric acid; a white precipitate of lead sulphate is produced.</td><td colspan="2">Residue may consist of **mercurous** and **silver chlorides.** Digest residue with ammonia water.</td></tr>
<tr><td>Solution may contain **silver.** Neutralize with nitric acid, when silver chloride is re-precipitated.</td><td>A dark gray residue indicates **mercury,** the white mercurous chloride having been converted into di-mercurous ammonium chloride.</td></tr>
</table>

Treatment of the precipitate formed by hydrogen sulphide in warm acid solution. The precipitate is collected upon a small filter, well washed with water, and then examined for its solubility in ammonium sulphide. This is done by placing a portion of the washed precipitate in a test-tube, adding ammonium sulphide, and warming gently. It is either wholly insoluble (metals of the lead group), and treated according to Table IV., or fully soluble (metals of the arsenic group), and treated according to Table V., or it is partly soluble and partly insoluble (metals of both groups). In the latter case, the total quantity of the washed precipitate is to be treated with warm ammonium sulphide; upon filtering, an insoluble residue is left, which is treated according to Table IV.; to the fil-

QUESTIONS.—321. State the three groups of heavy, and the three groups of light metals. 322. By which two reagents may all heavy metals be precipitated? 323. Why is a solution acidified before the addition of hydrogen sulphide, when testing for metals? 324. Which metals are precipitated by hydrochloric acid? 325. Which two groups of metals are precipitated by hydrogen sulphide in acid solution? 326. How are the sulphides of the arsenic group separated from those of the lead group? 327. Why is an acid solution neutralized or supersaturated by ammonium hydroxide, before adding ammonium sulphide? 328. Which two groups of metals are precipitated by ammonium sulphide, and in what forms of combination? 329. Name the group-reagent for the alkaline earths. 330. Which metals may be left in solution after hydrogen sulphide, ammonium sulphide, and ammonium carbonate have been added?

trate, diluted sulphuric acid is added as long as a precipitate is formed, which precipitate contains the metals of the arsenic group as sulphides, generally with some sulphur from the ammonium sulphide.

TABLE IV.—Treatment of that portion of the hydrogen sulphide precipitate which is insoluble in ammonium sulphide.

<table>
<tr><td colspan="4">The precipitate may contain the **sulphides of lead, copper, mercury, bismuth,** and **cadmium.** Heat the *well-washed* precipitate with nitric acid in a test-tube, and filter.</td></tr>
<tr><td rowspan="3">Residue may con- consist of:
Mercuric sulphide, which is black and easily dissolves in nitro-hydrochloric acid, which solution, after sufficient evaporation, is tested by potassium iodide, etc.
Lead sulphate is white, pulverulent, and soluble in ammonium tartrate.
Sulphur is yellow and combustible.</td><td colspan="3">Filtrate may contain the **nitrates of lead, copper, bismuth,** and **cadmium.** Add to the solution a few drops of dilute sulphuric acid.</td></tr>
<tr><td rowspan="2">Precipitated is **lead**, as white lead sulphate which is soluble in ammonium tartrate with excess of ammonium hydroxide.</td><td colspan="2">Solution may contain **copper, bismuth,** and **cadmium.** Supersaturate with ammonium hydroxide.</td></tr>
<tr><td>Precipitated is white **bismuth** hydroxide.
Dissolve in hydrochloric acid and apply tests for bismuth.</td><td>Solution may contain **copper** and **cadmium.**
Divide solution in two parts, and test for copper by potassium ferrocyanide in the acidified solution; a red precipitate indicates **copper.** To second part add potassium cyanide and hydrosulphuric acid. A yellow precipitate indicates **cadmium.**</td></tr>
</table>

TABLE V.—Treatment of the hydrogen sulphide precipitate which is soluble in ammonium sulphide.

<table>
<tr><td colspan="2">The precipitate may contain the **sulphides of arsenic, antimony, tin,** and a few of those metals which are but rarely met with in qualitative analysis, such as **gold, platinum, molybdenum,** and others, which latter metals, if suspected, may be detected by special tests.
Boil the washed precipitate with strong hydrochloric acid.</td></tr>
<tr><td>An insoluble yellow residue consists of **arsenous sulphide.**
The residue is dissolved by boiling with hydrochloric acid and a little potassium chlorate, and the solution examined by Fleitmann's test.
A dark-colored residue may indicate gold or platinum, for which use special tests.</td><td>The solution may contain the **chlorides of antimony** and **tin.**
The solution is introduced into Marsh's apparatus when all antimony is gradually evolved as antimoniuretted hydrogen, while tin remains with the undissolved zinc as a black metallic powder, which may be collected, washed, dissolved in hydrochloric acid, and the solution tested by the special tests for tin.</td></tr>
</table>

TABLE VI.—**Treatment of the precipitate formed by ammonium hydroxide and ammonium sulphide.**

<table>
<tr><td colspan="4">The precipitate may contain the sulphides of iron, manganese, and zinc (cobalt and nickel),[1] the hydroxides of chromium and aluminum, and possibly the phosphates of barium, calcium, strontium, and magnesium.[2]
Dissolve the washed precipitate in the smallest possible quantity of warm, dilute hydrochloric acid, and heat the solution with a few drops of nitric acid. To the clear solution add ammonium chloride, and supersaturate it with ammonium hydroxide.</td></tr>
<tr><td colspan="2">The precipitate may contain the hydroxides of iron, aluminum and chromium, and the phosphates of the alkaline earths or of magnesium. Dissolve the precipitate in a little hydrochloric acid, and supersaturate with potassium hydroxide.</td><td colspan="2">The solution may contain zinc, manganese, cobalt, and nickel. Acidulate the ammonia solution with acetic acid, and add hydrogen sulphide.</td></tr>
<tr><td>Precipitated is ferric hydroxide, reddish-brown. Dissolve in dilute hydrochloric acid, and add <i>potassium ferrocyanide.</i> A blue precipitate indicates iron.
Precipitate may also contain the <i>phosphates of the alkaline earths or magnesium.</i> To the solution of the precipitate in hydrochloric acid add ammonium hydroxide until a precipitate is formed which does not redissolve on stirring. Add a few drops of acetic acid to dissolve the precipitate, and then ammonium oxalate. A white precipitate indicates <i>calcium.</i>
<i>Barium and strontium</i> are indicated by the addition of calcium sulphate, and distinguished by flame reaction.
Test for phosphoric acid by ammonium molybdate.</td><td>Solution may contain aluminum, and, if green, chromium.
Supersaturate the alkaline solution slightly with hydrochloric acid, and add ammonium carbonate A white gelatinous precipitate indicates aluminum.
If the precipitate is green it may contain <i>chromium,</i> or <i>aluminum</i> and <i>chromium.</i> Separate as follows: Dissolve the washed precipitate in the smallest possible quantity of nitric acid, evaporate solution in porcelain dish nearly to dryness, add about two volumes of strong nitric acid and fragments of potassium chlorate; heat until solution has assumed a bright orange color. Dilute with water and supersaturate with ammonia; a white precipitate indicates <i>aluminum.</i> To filtrate add barium chloride; a yellow precipitate indicates <i>chromium.</i></td><td>Precipitate may contain the sulphides of zinc, cobalt, and nickel.
If the precipitate be white, it is zinc sulphide only; if black, it may contain cobalt and nickel If the latter be present, the precipitate is dissolved in hydrochloric acid with little nitric acid, and the solution supersaturated with potassium hydroxide. The filtrate then contains the zinc, the black precipitate cobalt and nickel.</td><td>Solution may contain manganese, which is verified by adding ammonium hydroxide and sulphide, which produce a flesh-colored precipitate.</td></tr>
</table>

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[1] The sulphides of cobalt and nickel are but sparingly soluble in hydrochloric acid, but dissolve readily in nitro-hydrochloric acid.

[2] In the absence of a sufficient quantity of ammonium chloride some magnesium hydroxide may also be precipitated.

The precipitation of sulphur, in the absence of metals of the arsenic group, frequently leads beginners to the assumption that metals of this group are present. The precipitate consisting only of sulphur is white and milky, but flocculent, and more or less colored in the presence of the metals of the arsenic group.

TABLE VII.—Treatment of the precipitate formed by ammonium carbonate.

The precipitate may contain the **carbonates of barium, calcium, and strontium.**[1] Dissolve the precipitate in acetic acid, and add potassium dichromate.

Precipitated is **barium**, as pale yellow **barium chromate.**	Solution may contain **calcium and strontium**. Neutralize solution with ammonia water and add potassium chromate.	
	Precipitated is **strontium**, as pale yellow **strontium chromate.**	Solution may contain **calcium**. Add ammonium oxalate: a white precipitate indicates **calcium**.

TABLE VIII.—Detection of the alkalies and of magnesium.

The fluid which has been treated with hydrochloric acid, hydrogen sulphide, ammonium hydroxide, sulphide, and carbonate, may contain **magnesium and the alkalies.**

Divide solution into two portions.

To the first portion add sodium phosphate. A white crystalline precipitate indicates **magnesium**.[2]

The second portion is evaporated to dryness, further heated (or ignited) until all ammonium compounds are expelled, and white fumes are no longer given off. The residue is dissolved in water, and sodium cobaltic nitrite added. A yellow precipitate indicates **potassium**. The residue is also examined by flame test: a yellow color indicating **sodium**, a red color **lithium.**

Ammonium compounds have to be tested for in the original fluid by treating it with calcium hydroxide, when ammonia gas is liberated

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[1] If an insufficient quantity of ammonium chloride should have been present, some magnesia may also be contained in this precipitate, and may be redissolved by treating it with ammonium chloride solution.

[2] If an insufficient quantity of ammonium chloride has been produced in the original solution by the addition of hydrochloric acid and ammonium hydroxide, a portion of the magnesia may have been precipitated by the ammonium hydroxide or carbonate.

QUESTIONS.—331. By what tests can mercurous chloride be distinguished from the chloride of silver or lead? 332. How can it be proved that a precipitate produced by hydrogen sulphide in an acid solution contians a metal

35. DETECTION OF ACIDS.

General remarks. There are no general methods (similar to those for the separation of metals) by which all acids can be separated, first into different groups, and afterward into the individual acids. It is, moreover, impossible to render all acids soluble (when in combination with certain metals) without decomposition, as, for instance, in the case of carbonic acid when in combination with calcium; calcium carbonate is insoluble in water, and when the solution is attempted by means of acids, decomposition takes place with liberation of carbon dioxide. Many other acids suffer decomposition in a similar manner, when attempts are made to render soluble the substances in which they occur.

It is due to these facts that a complete separation of all acids is not so easily accomplished as the separation of metals. There is, however, for each acid a sufficient number of characteristic tests by which it may be recognized; moreover, the preliminary examination, as well as the solubility of the substance, and the nature of the metal or metals present, will aid in pointing out the acid or acids which are present.

If, for instance, a solid substance be completely soluble in water, and if the only metal found were iron, it would be unnecessary to test for carbonic, phosphoric, and hydrosulphuric acids, because the combinations of these acids with iron are insoluble in water; there might, however, be present sulphuric, hydrochloric, nitric, and many other acids, which form soluble salts with iron.

Detection of acids by means of the action of strong sulphuric acid upon the dry substance. The action of sulphuric acid upon a dry powdered substance often furnishes such characteristic indica-

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or metals of either the arsenic or lead group? 333. How can mercuric sulphide be separated from the sulphides of copper and bismuth? 334. How does ammonium hydroxide act on a solution containing bismuth and copper? 335. State the action of strong, hot hydrochloric acid on the sulphides of arsenic and antimony. 336. Suppose a solution to contain salts of iron, aluminum, zinc, and manganese; by what process could these four metals be separated and recognized? 337. How can barium, calcium, and strontium be recognized when dissolved together? 338. By what tests is magnesium recognized? 339. State a method of separating potassium when mixed with other metallic compounds. 340. How are ammonium compounds recognized when in solution with other metals?

tions of the presence or absence of certain acids, that this treatment should never be omitted when a search for acids is made.

When the substance under examination is liquid, a portion should be evaporated to dryness, and, if a solid residue remains, it should be treated in the same manner as a solid.

Most non-volatile, organic substances (including most organic acids) color sulphuric acid dark when heated with it.

Dry inorganic salts when heated with sulphuric acid either are decomposed, with liberation of the acid (which may escape in the gaseous state), or with liberation of volatile products (produced by the decomposition of the acid itself), or no apparent action takes place. See Table IX.

Detection of acids by means of reagents added to their neutral or acid solution. Whenever a substance is soluble in water, there is little difficulty of finding the acid by means of Table X.; but if the substance is insoluble in water, and has to be rendered soluble by the action of acids, this table may, in some cases, be of no use, because the acid originally present in the substance may have been liberated, and escaped in a gaseous state (as, for instance, when dissolving insoluble carbonates in acids), or the tests mentioned in the table may refer to neutral solutions, while it is impossible to render the solution neutral without re-precipitating the dissolved acid. If calcium phosphate, for instance, be dissolved by hydrochloric acid, the magnesium test for phosphoric acid cannot be used, because this test can be applied to a neutral or an alkaline solution only; in attempting, however, to neutralize the hydrochloric acid solution, calcium phosphate itself is re-precipitated.

Table XI., showing the solubility or insolubility (in water) of over 300 of the most important inorganic salts, oxides, and hydroxides, will greatly aid the student in studying this important feature. It will also guide him in the analysis of inorganic substances, as it gives directions for over 300 (positive or negative) tests for metals, and an equal number for acids.

To understand this, it must be remembered that any salt (or oxide or hydroxide) which is insoluble in water may be produced and precipitated by mixing two solutions, one containing the metal, the other containing the acid of the insoluble salt to be formed. For instance: Table XI. states that the carbonates of most metals are insoluble in water. To produce, therefore, the carbonate of any of these metals (zinc, for instance) it becomes necessary to add to any solution of zinc (sulphate, chloride, or nitrate of zinc) any soluble carbonate (sodium or potassium carbonate), when the insoluble zinc carbonate is produced.

Soluble carbonates consequently are reagents for soluble zinc salts, while at the same time soluble zinc salts are reagents for soluble carbonates.

For similar reasons soluble zinc salts are, according to Table XI., reagents for soluble phosphates, arsenates, arsenites, hydroxides, and sulphides, but not for iodides, chlorides, sulphates, nitrates, or chlorates.

The insolubility of a compound in water is not an absolute guide for preparing this compound according to the general rule given above for the precipitation of insoluble compounds, there being some exceptions.

For instance: Cupric hydroxide is insoluble in water; therefore, by adding solution of cupric sulphate to any soluble hydroxide, the insoluble cupric hydroxide should be precipitated, and is precipitated by the soluble hydroxides of potassium and sodium, but not permanently by the soluble hydroxide of ammonium, on account of the formation of the soluble ammonium cupric sulphate.

There are not many such exceptions, and to mention them in the table would have greatly interfered with its simplicity, for which reason they have been omitted.

For the same reason some compounds, which are not known at all, have not been specially mentioned. For instance, according to Table XI., aluminum carbonate and chromium carbonate are insoluble salts: actually, however, these compounds can scarcely be formed, the affinity between the weak carbonic acid and the feeble bases not being sufficient to unite them.

Finally, it may be stated that no well-defined line can be drawn between soluble and insoluble substances. There is scarcely any substance which is not slightly soluble in water, and many of the so-called soluble substances are but very sparingly soluble, as, for instance, the hydroxide and sulphate of calcium.

Table XII. shows the solubility of a large number of compounds more accurately than Table XI.; it may be used for reference.

TABLE IX.—Preliminary examination for inorganic acids.

A small quantity of the finely powdered substance is treated with about four times its weight of **concentrated sulphuric acid**, in a test-tube, care being taken not to heat to the boiling-point of sulphuric acid.

No apparent change takes place. **No gas is evolved.**	**A colorless gas is evolved.**	**A colored gas is evolved.**
Sulphuric acid (hepar and barium test). **Phosphoric acid** (molybdate of ammonium test). **Boric acid** (green flame after moistening with sulphuric acid). **Arsenic acid,** **Silicic acid,** **Molybdic acid,** **Phosphorous acid,** **Arsenous acid,** } Special tests.	**Hydrochloric acid** (silver test). **Carbonic acid** (the gas is generated also by diluted acids in the cold, and renders lime-water turbid). **Nitric acid** (the vapors turn red on the addition of ferrous sulphate). **Sulphurous acid** (odor). **Hydrosulphuric acid** (odor). **Hydrofluoric acid** (corrodes glass). **Acetic acid** (odor of acetic ether on the addition of alcohol). **Many organic acids** are decomposed with liberation of colorless gases.	**Hydriodic acid** (violet vapors of iodine). **Hydrobromic acid** (brown vapors of bromine). **Bromic acid** (brown vapors; deflagration on charcoal). **Chloric acid** (the greenish-yellow gas explodes readily). **Nitric acid** (vapors more red on adding ferrous sulphate). **Nitrous acid** (red vapors).

Whenever one or more acids are suspected or are indicated by the above tests, their presence is to be verified by the tests in Tables X and XI., or by the reactions given in connection with the consideration of the acids themselves. For latter tests see Index.

TABLE X.—Detection of the more important acids by means of reagents added to the solution.

Barium chloride precipitates:	**Calcium chloride** precipitates from *neutral* or *alkaline* solution:	**Ferric chloride** precipitates from *neutral* solution:	**Magnesium sulphate** precipitates in the presence of **ammonium hydroxide and chloride**:	**Silver nitrate** precipitates	
				from *neutral* solution:	from *neutral* or *acid* solution:
Sulphuric acid, white.	**Sulphuric acid,** white.	....	....	....	**Hydrochloric acid,** white.
Sulphurous acid, white.	**Sulphurous acid,** white.	....	....	**Sulphurous acid,** white.	**Hydrobromic acid,** white.
Phosphoric acid, white.	**Phosphoric acid,** white.	**Phosphoric acid,** yellowish-white.	**Phosphoric acid,** white.	**Phosphoric acid,** pale yellow.	**Hydriodic acid,** white.
Phosphorous acid, white.	....	....	....	**Phosphorous acid,** white, then black.	**Iodic acid,** white.
Carbonic acid, white.	**Carbonic acid,** white.	(Ferric hydroxide is precipitated and carbon dioxide escapes.)	....	**Carbonic acid,** white.	**Hydrocyanic acid,** white.
Boric acid, white.	**Boric acid,** white.	**Boric acid,** yellowish.	....	**Boric acid,** white.	**Ferrocyanides,** white.
Arsenic acid, white.	**Arsenic acid,** white.	**Arsenic acid,** yellowish-white.	**Arsenic acid,** white.	**Arsenic acid,** brownish red.	**Ferricyanides,** reddish-brown.
Arsenous acid, white.	....	**Ferrocyanides,** blue.	....	**Arsenous acid,** yellow.	**Sulphocyanides,** white.
Chromic acid, pale yellow.	....	**Sulphocyanides,** red coloration.	....	**Chromic acid,** red.	**Hydrosulphuric acid,** black.
....	....	**Hydrosulphuric acid,** black.	....	....	
Oxalic acid, white.	**Oxalic acid,** white.	**Oxalic acid,** yellow.	....	**Oxalic acid,** white.	Not precipitated are:
Tartaric acid, white.	**Tartaric acid,** white.	**Tannic acid,** black.	**Tartaric acid,** white; precipitate forms slowly.	**Tartaric acid,** white.	**Nitric acid.**
Citric acid, white.	**Citric acid,** white.	**Acetic acid,** a reddish-brown coloration is produced, and, on boiling, a reddish-brown precipitate.	....	**Citric acid,** white.	**Nitrous acid.**
All the above precipitates are soluble in hydrochloric and most other acids, with the exception of barium sulphate.					**Chloric acid.**
					Hypochlorous acid.
					Acetic acid.

36. METHODS FOR QUANTITATIVE DETERMINATIONS.

General remarks. Quantitative determination of the different elements or groups of elements may be accomplished by various methods, which differ generally with the nature of the substance to be examined. But even one and the same substance may often be analyzed quantitatively by entirely different methods, of which the two principal ones are the *gravimetric* and *volumetric* methods.

In the *gravimetric method*, the quantities of the constituents of a substance are determined by separating and weighing them either as such, or in the form of some compound the exact composition of which is known. For instance: From cupric sulphate, the copper may be precipitated as such by electrolysis and weighed as metallic copper, or it may be precipitated by sodium hydroxide as cupric oxide, CuO, and weighed as such. Knowing that every 79.2 parts by weight of cupric oxide contain of oxygen 16 parts and of copper 63.2 parts, the weight of copper contained in the cupric oxide found may be readily calculated.

In the *volumetric method*, the determination is accomplished by adding to a weighed quantity of the substance to be examined, a solution of a reagent of a known strength until the reaction is just completed, no excess being allowed. For instance: We know that every 80 parts by weight of sodium hydroxide precipitate 79.2 parts by weight of cupric oxide, containing 63.2 parts by weight of copper. Therefore, if we add a solution of sodium hydroxide of known strength to a weighed portion of cupric sulphate until all the copper is precipitated,

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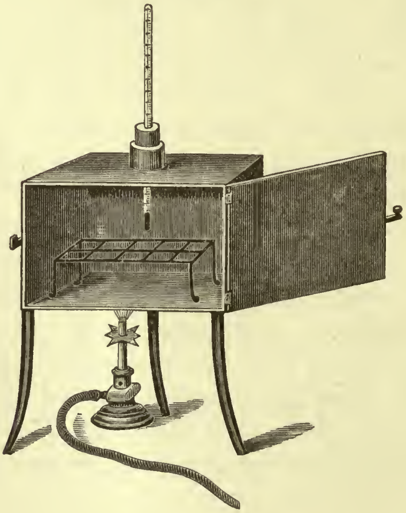
QUESTIONS.—341. Why is sulphuric acid added to a solid substance when it is to be examined for acids? 342. Mention some acids which cause the liberation of colorless, and some which cause the liberation of colored gases when the salts of these acids are heated with sulphuric acid. 343. Mention an acid which is precipitated by barium chloride in acid solution, and some acids which are precipitated by the same reagent in neutral solution. 344. Which acids may be precipitated by silver nitrate from neutral solutions, and which from either neutral or acid solutions? 345. Mention some acids which form soluble salts only. 346. Mention three soluble, and three insoluble carbonates, phosphates, arsenates, sulphates, and sulphides respectively. 347. Which oxides or hydroxides are soluble, and which are insoluble in water? 348. Mention some metals, the solutions of which are precipitated by soluble chlorides, iodides, and sulphides. 349. State a general rule according to which most insoluble salts may be formed from two other compounds. 350. Why is it sometimes impossible to render a substance soluble in order to test for the acid in the solution obtained?

we may calculate from the volume of soda solution used the weight of sodium hydroxide, and from this the weight of copper which has been precipitated. The operation of volumetric analysis is termed *titration.*

Gravimetric methods. While the quantitative determinations by these methods differ widely in some cases, there are a number of operations so often and so generally employed that a few remarks may be of advantage to the beginner. A small quantity (generally from 0.5 to 1 gramme) of the substance to be analyzed is very exactly weighed on a delicate balance, transferred to a beaker, and dissolved in a suitable agent (water or acid). From this solution the constituent to be determined is precipitated completely, which is ascertained by allowing the precipitate to subside and adding to the clear liquid a few drops more of the agent used for precipitation. The precipitate is next collected upon a small filter of good filter paper containing as little of inorganic constituents (ash) as possible; the particles of precipitate which may adhere to the beaker are carefully washed off by means of a camel's-hair brush. The precipitate is well washed (generally with pure water) until free from adhering solution, and dried by placing funnel and contents in a drying-oven, Fig. 28, in which a constant temperature of about 100° C. (212° F.) is maintained. The dried filter is then taken from the funnel and its contents are transferred to a platinum (or porcelain) crucible, which has been previously

FIG. 28.



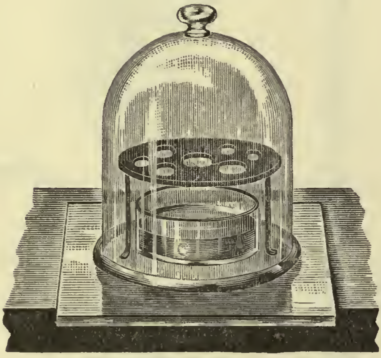
Drying-oven.

weighed and stands on a piece of glazed, colored paper in order to collect any particle of the dried precipitate which may happen to fall beside the crucible. The filter, from which the precipitate has been removed as completely as possible, by slightly rubbing it, is now folded, placed upon the lid of the crucible, which rests on a triangle over a gas-burner, and completely incinerated. The remaining filter-ash, with particles of the precipitate mixed with it, is transferred to the crucible, which is now placed over the burner and heated until all water (or possibly other substances) is completely expelled. After cooling, the crucible is weighed, the weight of the empty crucible and that of the filter-ash (the latter having been previously determined by burning a few filters of the same kind) deducted, and thus the quantity of the precipitate determined.

As platinum crucibles and many precipitates, after ignition, absorb moisture from the air, it is well to allow the heated crucible to cool in a *desiccator*. This is a closed vessel in which the contained air is kept dry by means of concentrated sulphuric acid. Fig. 29 shows a convenient form of desiccator.

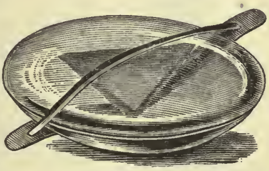
The empty crucibles should be weighed under the same conditions —*i. e.*, after having been heated and cooled in a desiccator.

FIG. 29.



Desiccator.

FIG. 30.



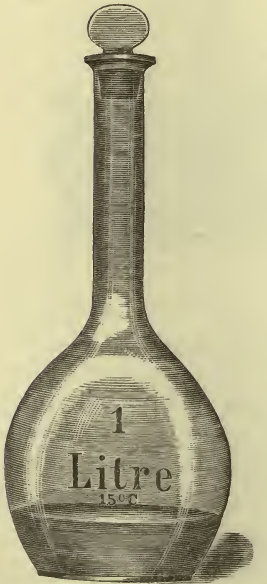
Watch-glasses for weighing filters.

Some precipitates (as, for instance, potassium platinic chloride), cannot be ignited without suffering partial or complete decomposition. It is for this reason that some precipitates are collected upon filters which have been previously dried at 100° C. (212° F.) and weighed carefully. The precipitate is then collected upon the weighed filter, well washed, dried at 100° C. (212° F.) and weighed.

The weighing of dried filters is best accomplished by placing them between two watch-glasses held together by means of a brass or nickel clamp, as shown in Fig. 30.

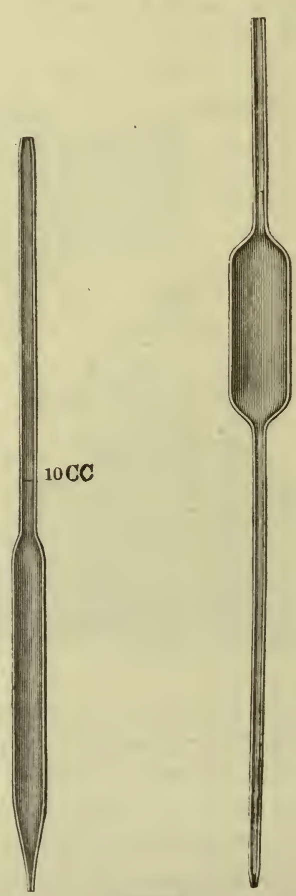
The above-described methods may be employed for the determination of those substances which can be precipitated from their solutions in the form of some stable compound. Aluminum, zinc, iron, bismuth, copper, etc., may, for instance, be precipitated as hydroxides and weighed as oxides, into which the precipitated compound is converted by ignition. Sulphuric acid may be precipitated and weighed as barium sulphate, phosphoric acid may be precipitated by magnesia mixture and weighed as magnesium pyrophosphate, etc. Some substances, like nitric acid, chloric acid, etc., cannot be precipitated from their solutions, for which reason other methods have to be employed for their determination.

FIG. 31.



Liter flask.

FIG. 32.

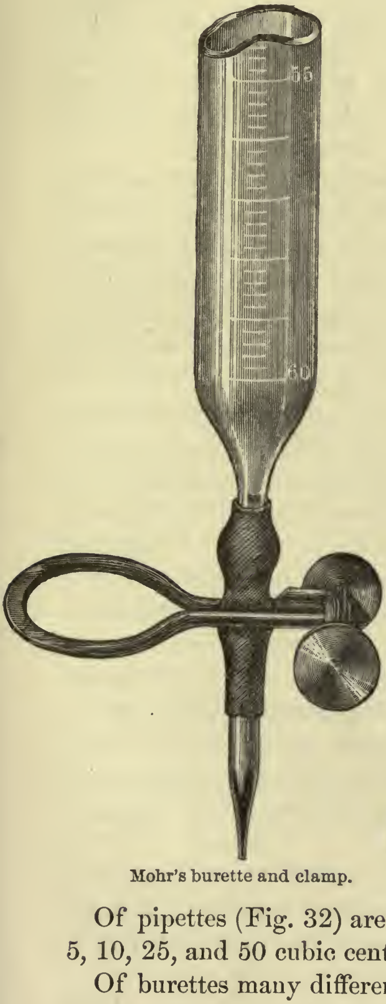


Pipettes.

Volumetric methods. The great advantage of volumetric over gravimetric analysis consists chiefly in the rapidity with which these determinations are performed. Unfortunately, volumetric methods cannot be employed to advantage for the estimation of all substances.

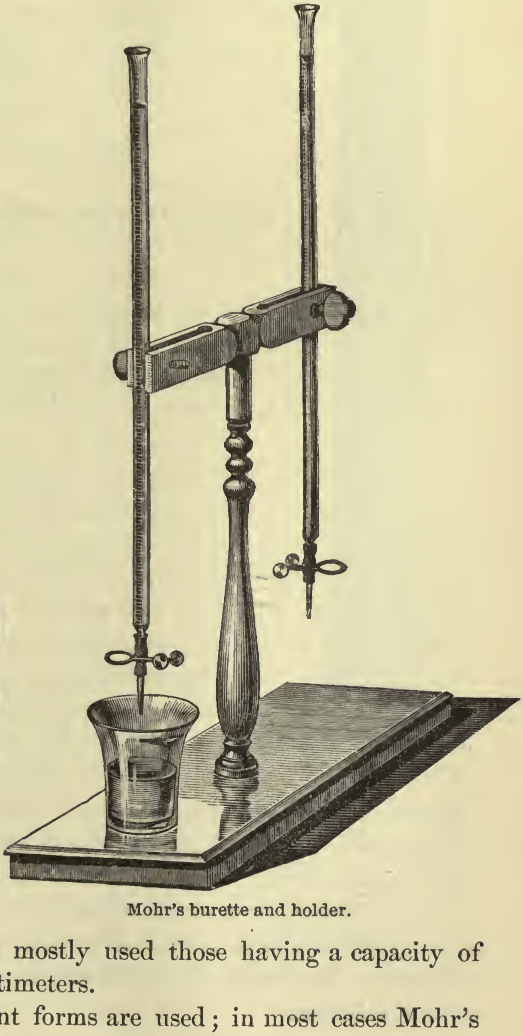
The special apparatus required for volumetric analysis consists of a few flasks, some pipettes, burettes, and a burette-holder. The flasks should have a mark on the neck, indicating a capacity of 100, 250, 500, and 1000 c.c. respectively. (See Fig. 31.)

FIG. 33.



Mohr's burette and clamp.

FIG. 34.

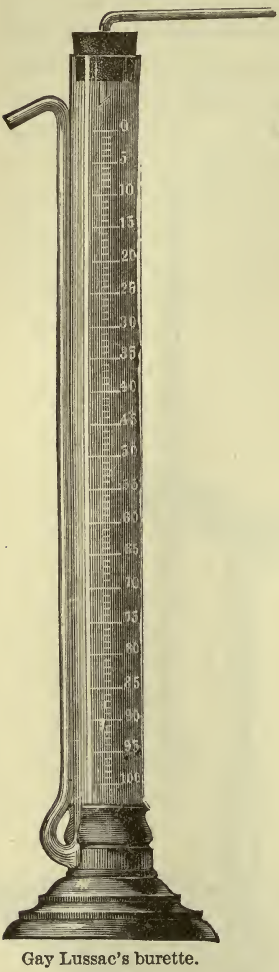


Mohr's burette and holder.

Of pipettes (Fig. 32) are mostly used those having a capacity of 5, 10, 25, and 50 cubic centimeters.

Of burettes many different forms are used; in most cases Mohr's burette (Figs. 33 and 34) answers all requirements, but its application is excluded whenever the test solution is chemically affected by rubber, as in the case of solutions of silver, permanganate, and a few other substances. For such solutions Mohr's burette with glass stopcock, or Gay Lussac's burette (Fig. 35) is generally used.

Fig 35.



Gay Lussac's burette.

Standard solutions. The test solutions used in volumetric analysis are adjusted according to a uniform system, so that each solution contains in a liter (1000 c.c.) the weight of one atom or one molecule of the active reagent expressed in grammes. This rule refers to all cases of univalent elements (Ag, Cl, I), or monobasic acids (HCl, HNO_3), or monacid bases (KOH, NH_4OH). In case a bivalent element (O, S), or di-basic acids (H_2SO_4, $H_2C_2O_4$), or diacid bases [$Ca(OH)_2$], are used in volumetric solutions, only one-half of the atomic or molecular weight in grammes is used per liter, so as to have the saturating or neutralizing power the same for an equal number of cubic centimeters of univalent and bivalent substances.

To illustrate why this is done, if we were to take the molecular weight of hydrochloric acid, 36.4, and of sulphuric acid, 98, in grammes, diluted to 1000 c.c., the saturating power of 1 c.c. of the diluted sulphuric acid would be equal to that of 2 c.c. of hydrochloric acid solution, because 36.4 parts by weight of hydrochloric acid saturate 40 parts by weight of sodium hydroxide, and 98 parts by weight of sulphuric acid saturate 80 parts by weight of sodium hydroxide.

The solutions thus obtained are known as *normal solutions.* For some operations these normal solutions are too concentrated, and are diluted to one-tenth of their strength, and are then called *decinormal solutions.*

Normal solutions are generally designated by $\frac{N}{1}$, deci-normal solutions by $\frac{N}{10}$, centi-normal solutions by $\frac{N}{100}$; solutions containing twice the amount are designated as double normal, $\frac{2}{N}$; half the amount semi-normal, $\frac{N}{2}$.

In some instances volumetric solutions are prepared which do not belong to the above system of normal solutions, but are adjusted to correspond to a certain unit of the special substance they are to act upon. Such solutions are called *empirical solutions;* as an instance may be mentioned Fehling's solution, used for the determination of sugar. This solution is so adjusted that 1 c.c. decomposes or indicates 0.005 gramme of grape-sugar.

Different methods of volumetric determination. Of these we have at least three, which may be called the direct, the indirect, and the method of rest or residue.

The *direct methods* are used in all cases in which the quantities of volumetric solutions can be added until the reaction is complete: for instance, until an alkaline substance has been neutralized by an acid, or a ferrous salt has been converted into a ferric salt by potassium permanganate, etc.

In the *indirect methods* one substance, which cannot well be determined volumetrically, is made to act upon a second substance, with the result that, by this action, an equivalent amount of a substance is generated or liberated, which may be titrated. For instance: Peroxides, chromic and chloric acids when boiled with strong hydrochloric acid, liberate chlorine, which is not determined directly, but is caused to act upon potassium iodide, from which it liberates the iodine, which may be titrated with sodium thiosulphate.

The *methods of residue* are based upon the fact that while it is impossible or extremely difficult to obtain complete decomposition between certain substances and reagents, when equivalent quantities are added to one another, such a complete decomposition is accomplished by adding an excess of the reagent, which excess is afterward determined by a second volumetric solution. For instance: Carbonate of calcium, magnesium, zinc, etc., cannot well be determined directly, for which reason an excess of normal acid is used for their decomposition, this excess being titrated afterward by means of an alkali.

Indicators. In all cases of volumetric determination it is of the greatest importance to observe accurately the completion of the reaction. In some cases the final point is indicated by a change in color, as, for instance, in the case of potassium permanganate, which changes from a red to a colorless solution, or chromic acid, which changes from orange to green under the influence of deoxidizing agents. In other cases the determination is indicated by the formation or cessation of a precipitate, and in yet others the final point could not be noticed with precision unless rendered visible by a third substance added for that purpose.

Such substances are termed *indicators.* Litmus, phenol-phtalein, methyl-orange, etc., are used as indicators in acidimetry and alkalimetry. Starch paste is an indicator for iodine, potassium chromate for silver, etc. Of indicators, a few drops are in most cases sufficient for the purpose.

Litmus solution. This is made by exhausting coarsely powdered litmus with boiling alcohol, which removes a red coloring matter, erythrolitmin. The residue is treated with about an equal weight of cold water, so as to dissolve the excess of alkali present in litmus. The remaining mass is extracted with about five times its weight of boiling water, and filtered. The solution should be kept in wide-mouthed bottles, stoppered with loose plugs of cotton to exclude dust but to admit air. *Blue* and *red litmus paper* is made by impregnating strips of unsized white paper with the blue solution obtained by the above process, or with this solution after just enough hydrochloric acid has been added to impart to it a distinct red tint.

Phenol-phtalein solution. 1 gramme of phenol-phtalein is dissolved in 100 c.c. of diluted alcohol. The colorless solution is colored deep purplish-red by alkali hydrates or carbonates, but not by bicarbonates; acids render the red solution colorless. The solution is not suitable as an indicator for ammonia or bicarbonates.

Methyl-orange solution. 1 gramme of methyl-orange (also known as helianthin, tropæolin D, or Poirier's orange III), dimethylamido-azobenzol-sulphonic acid, $(CH_3)_2N.C_6H_4.N.NC_6H_4.SO_3H$, is dissolved in 1000 c.c. of water. The solution is yellow when in contact with alkaline hydrates, carbonates, or bicarbonates. Carbonic acid does not affect it, but mineral acids change its color to crimson.

Rosolic acid solution. 1 gramme of commercial rosolic acid (chiefly $C_{20}H_{16}O_3$) is dissolved in 10 c.c of alcohol, and water added to make 100 c.c. The solution turns violet-red with alkalies, yellow with acids.

Other indicators used at times in acidimetry are solutions of brazil-wood, cochineal, corallin, eosin, fluorescein, turmeric, etc.

Titration. This term is used for the process of adding the volumetric solution from the burette to the solution of the weighed substance until the reaction is completed. We also speak of the *standard* or *titer* of a volumetric test-solution, when we refer to its strength per volume (per liter or per cubic centimeter).

Of the principal processes of titration, or of volumetric methods used, may be mentioned those based upon *neutralization* (acidimetry and alkalimetry), *oxidation and reduction* (permanganates and chromates as oxidizing, oxalic acid and ferrous salts as reducing agents) *precipitation* (silver nitrate by sodium chloride), and finally those which depend on the *action of iodine* and *hyposulphite* (iodimetry).

Acidimetry and alkalimetry. Preparing the volumetric test-solutions is often more difficult than to make a volumetric determination. Whenever the reagents employed can be obtained in a chemically pure condition it is an easy task to prepare the solution, because a definite weight of the reagent is dissolved in a definite volume of water. In many instances, however, the reagent cannot be obtained absolutely pure, and in such cases a solution is made and its standard adjusted afterward by methods which will be spoken of later.

Neither the common mineral acids, such as sulphuric, hydrochloric, and nitric acids, nor the alkaline substances, such as sodium hydroxide or ammonium hydroxide, are sufficiently pure to permit of being used directly for volumetric solutions, because these substances contain water, and an absolutely correct determination of the amount of this water is an operation which involves a knowledge of gravimetric methods.

It is for this reason that the basis in preparing a volumetric normal acid solution is oxalic acid, a substance which can be readily obtained in a pure crystallized condition.

Normal acid solution. Crystallized oxalic acid has the composition $H_2C_2O_4.2H_2O$ and a molecular weight of 125.7. Being dibasic, only half of its weight is taken for the normal solution, which is made by placing 62.85 grammes of pure crystallized oxalic acid in a liter flask, dissolving it in pure water, filling up to the mark at the temperature of 15° C. (59° F.) and mixing thoroughly.

Normal solutions of sulphuric or hydrochloric acid are, for various reasons, often preferred to oxalic acid. These solutions are best made by diluting approximately the acids named, titrating the solution with normal sodium hydroxide, using phenol-phtalein as an indicator, and adding water until equal volumes saturate one another. For instance, if it should be found that 10 c.c. normal alkali solution neutralize 7.6 c.c. of the acid, then 24 c.c. of water have to be added to every 76 c.c. of the acid in order to obtain a normal solution. Normal sulphuric acid contains 48.91 grammes of H_2SO_4, and normal hydrochloric acid 36.37 grammes of HCl per liter.

These normal solutions can be made conveniently by diluting either 30 c.c. of pure, concentrated sulphuric acid of sp. gr. 1.84, or 130 c.c. of hydrochloric acid of sp. gr. 1.16 to 1000 c.c. The solutions thus obtained are yet too concentrated and are adjusted as described above.

Other methods of determining the exact standard of normal acids depend upon the precipitation of 10 c.c. of the sulphuric acid solution by barium chloride, or of 10 c.c. of the hydrochloric acid solution by silver nitrate, and weighing the precipitated barium sulphate or silver chloride. Ten c.c. of normal sulphuric acid give 1.1736 gramme of barium sulphate, and 10 c.c. of normal hydrochloric acid 1.43 gramme of silver chloride.

A third method depends on the formation of, and the weighing as, an ammonium salt. Ten c.c. of either acid are neutralized (or slightly supersaturated) with ammonia water. The solution is evaporated in a previously weighed platinum dish over a water-bath, the dry salt is repeatedly moistened with alcohol, and finally dried in an air-bath at a temperature of 105° C. (221° F.) for about half an hour. Ten c.c. of normal sulphuric acid give of ammonium sulphate 0.6592 gramme, and 10 c.c. of normal hydrochloric acid of ammonium chloride 0.5338 gramme.

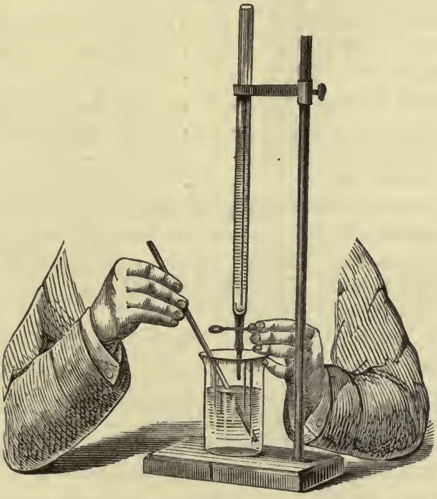
Normal alkali solution. A normal solution of sodium carbonate may be made by dissolving 52.92 grammes (one-half the molecular weight) of pure sodium carbonate (obtainable by heating pure sodium bicarbonate to a low red-heat) in water, and diluting to one liter. This solution, however, is not often used, but may serve for standardizing acid solutions, as it has the advantage of being prepared from a substance that can be easily obtained in a pure condition, which is not the case in preparing the otherwise more useful *normal solutions of potassium or sodium hydroxide*, both of which substances contain and absorb water.

The solutions are made by dissolving about 60 grammes of potassium hydroxide or 50 grammes of sodium hydroxide in about 1000 c.c. of water, titrating this solution with normal acid, and diluting it with water, until equal volumes of both solutions neutralize one another exactly.

The indicators used in alkalimetry are chiefly solution of litmus or phenol-phtalein, only a few drops of either solution being needed for a determination.

Whenever carbonates are titrated with acids, or *vice versa*, the solution has to be boiled toward the end of the reaction in order to drive off the carbon dioxide, as neither of the two indicators mentioned gives reliable results in the presence of carbonic acid or an acid carbonate. This boiling is unnecessary when methyl-orange is used, because it is not influenced by carbonic acid.

FIG. 36.



Titration.

The proper mode of performing the operation of titration is shown in Fig. 36.

When salts of organic acids with alkali metals are to be titrated with normal acids, these salts are first converted into carbonates. This is accomplished by igniting the weighed quantity of the salt in a crucible of porcelain or platinum. The chemical action which takes place during the ignition of potassium acetate may be shown thus:

$$2KC_2H_3O_2 + 8O = K_2CO_3 + 3H_2O + 3CO_2.$$

In a similar manner the alkali salts of all organic acids are converted into carbonates. Frequently some carbon is left unburned; this, however, does not interfere with the result of the titration. The titration is made with the liquid obtained by dissolving in water the residue left after ignition.

Neutralization equivalents. The normal solutions of acid and alkali may be used for the determination of a large number of substances, either directly (as in the case of free acids, caustic and alkaline carbonates and bicarbonates) or indirectly (as in the case of salts of most of the organic acids, with alkalies, which are first converted into carbonates by ignition).

One c.c. of normal acid is the equivalent of:

	Gramme.
Ammonia, NH_3	0.01701
Ammonium carbonate, $(NH_4)_2CO_3$	0.04293
Ammonium carbonate (U. S. P.), $NH_4HCO_3.NH_4NH_2CO_2$	0.05226
Lead acetate, crystallized $Pb(C_2H_3O_2)_2.3H_2O$ [1]	0.18900
Lead subacetate, $Pb_2O(C_2H_3O_2)_2$ [1]	0.13662
Lithium benzoate, $LiC_7H_5O_2$ [2]	0.12772
Lithium carbonate, Li_2CO_3 [2]	0.03693
Lithium citrate, $Li_3C_6H_5O_7$ [2]	0.06986
Lithium salicylate, $LiC_7H_5O_3$ [2]	0.14368
Potassium acetate, $KC_2H_3O_2$ [2]	0.09789
Potassium bicarbonate, $KHCO_3$	0.09988
Potassium bitartrate, $KHC_4H_4O_6$ [2]	0.18767
Potassium carbonate, K_2CO_3	0.06895
Potassium citrate, crystallized, $K_3C_6H_5O_7.H_2O$ [2]	0.10789
Potassium hydroxide, KOH	0.05599
Potassium permanganate, $KMnO_4$ [3]	0.03153
Potassium sodium tartrate, $KNaC_4H_4O_6.4H_2O$ [2]	0.14075
Potassium tartrate, $2K_2C_4H_4O_6.H_2O$ [2]	0.11734
Sodium acetate, $NaC_2H_3O_2.3H_2O$ [2]	0.13574
Sodium benzoate, $NaC_7H_5O_2$ [2]	0.14371
Sodium bicarbonate, $NaHCO_3$	0.08385
Sodium borate, crystallized, $Na_2B_4O_7.10H_2O$	0.19046
Sodium carbonate, crystallized, $Na_2CO_3.10H_2O$	0.14272
Sodium carbonate, Na_2CO_3	0.05292
Sodium hydroxide, NaOH	0 03996

One c.c. of normal sodium carbonate, potassium hydroxide, or sodium hydroxide, is the equivalent of:

	Gramme.
Acetic acid, $HC_2H_3O_2$	0.05986
Citric acid, crystallized, $H_3C_6H_5O_7.H_2O$	0.06983
Hydrobromic acid, HBr	0.08076
Hydrochloric acid, HCl	0.03637
Hydriodic acid, HI	0.12753
Hypophosphorous acid, HPH_2O_2	0.06588
Lactic acid, $HC_3H_5O_3$	0.08989
Nitric acid, HNO_3	0.06289
Oxalic acid, crystallized, $H_2C_2O_4.2H_2O$	0.06285
Phosphoric acid, H_3PO_4 (to form K_2HPO_4; with phenol-phtalein)	0.04890
Phosphoric acid, H_3PO_4 (to form KH_2PO_4; with methyl-orange)	0.09780
Potassium dichromate, $K_2Cr_2O_7$ (with phenol-phtalein)	0 14689
Sulphuric acid, H_2SO_4	0.04891
Tartaric acid, $H_2C_4H_4O_6$	0.07482

Oxidimetry. Potassium permanganate. The substances generally used as oxidizing agents are potassium permanganate and potassium dichromate, both of which salts can be obtained in a pure crystallized condition.

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[1] With sulphuric acid and methyl-orange.

[2] After ignition.

[3] With oxalic acid only.

Potassium permanganate, $KMnO_4 = 157.67$, acts generally in the presence of free acids, upon deoxidizing substances, by losing 5 atoms of oxygen of the 8 atoms contained in two molecules, as is shown in the following equations:

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$
$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_23SO_4 + 8H_2O.$$

It follows that two-fifths of the molecular weight of potassium permanganate, or 63.068 grammes, are the equivalent of 1 oxygen atom. But as oxygen is diatomic and the volumetric normal is calculated for monatomic values, this number must be divided by 2, and 31.534 grammes of pure crystallized potassium permanganate is therefore the amount to furnish 1 liter of normal solution, but as this is too concentrated for most determinations, a deci-normal solution containing 3.1534 grammes to the liter is generally employed.

Permanganate solution, when recently made, without observing certain precautions, will deteriorate for a certain length of time, *i. e.*, until all traces of organic and other deoxidizing matters have become oxidized by the permanganate.

In order to prepare permanent volumetric solutions of permanganate it is advisable to make two solutions, one too concentrated and the other too dilute for standard. These solutions are boiled and set aside in well-closed bottles for two days, in order to allow any precipitated matter to settle. By mixing the two solutions in the proper proportions a solution of the desired strength can be obtained, and as there is no longer any matter in the solution which can act decomposingly upon the permanganate the solution retains its standard for many months.

To prepare the two solutions necessary for deci-normal potassium permanganate solution, dissolve 3.5 grammes of potassium permanganate and 3 grammes in one liter of water each. Boil the solutions for a few minutes, set them aside for two days, and pour off the clear portions of each solution into separate vessels provided with glass stoppers.

To find the proportions in which these solutions have to be mixed in order to obtain a deci-normal solution the strength of each one has to be determined; this is done as follows: To a mixture of 10 c.c. of deci-normal oxalic acid solution and 1 c.c. of concentrated sulphuric acid, while yet hot, is added from a burette the weaker permanganate solution until it is no longer decolorized. In the same manner the titer of the stronger solution is determined.

Having ascertained the strength of each solution, the proportions for mixing them are ascertained by using the formula:

$$\underset{\text{Stronger solution.}}{(W-10)\,S.} \quad + \quad \underset{\text{Weaker solution.}}{(10-S.)\,W.}$$

By W are indicated the c.c. of weaker solution, by S the c.c. of stronger solution required to decompose 10 c.c. of deci-normal oxalic acid.

For instance: Assuming that 9.5 c.c. of the stronger (S) and 10.4 c.c. of the weaker (W) solution had been required, then, substituting these values in the above-given formula, we obtain:

$$(10.4-10)\,9.5 + (10-9.5)\,10.4,$$

or

$$3.8 \quad + \quad 5.2,$$

making 9 c.c. of final solution.

The bulk of the two solutions is now mixed in the same proportion, say 380 c.c. of the stronger and 520 c.c. of the weaker solution.

After the mixture is thus prepared, a new trial should be made, when equal volumes of the solution prepared and of deci-normal oxalic acid solution should exactly decompose one another. Instead of working with 10 c.c. of the solutions it is advisable to use larger quantities, say 20 or even 50 c.c., whereby the errors made by reading are diminished.

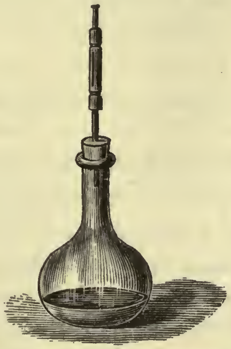
Instead of using oxalic acid for standardizing permanganate solution, metallic iron may be used, and the operation should be conducted as follows: 0.2 gramme of pure, thin iron wire is dissolved in about 20 c.c. of dilute sulphuric acid (1 acid, 5 water) by the aid of heat, and in a flask arranged as in Fig. 37. The flask is provided, by means of a perforated cork, with a piece of glass tubing, to which is attached a piece of rubber tubing in which is cut a vertical slit about one inch long and which is closed at the upper end by a piece of glass rod; gas or steam generated in the flask may escape, while atmospheric air cannot enter, the ferrous solution being thus protected from oxidation.

The iron solution, obtained from the 0.2 gramme of iron, is cooled and diluted with about 300 c.c. of water, and then deci-normal potassium permanganate solution is added with constant stirring until the solution is tinged pinkish.

As 1 c.c. of deci-normal permanganate solution corresponds to 0.005588 gramme of metallic iron, the 0.2 gramme of iron wire used will consume 35.7 c.c. of the solution.

Permanganate is often used in determinations of iron and iron compounds. Many of the latter contain iron in the ferric state, which must be converted into ferrous compounds before titration. This conversion is accomplished by heating the solution of a weighed quantity of the ferric compound with nascent hydrogen—*i. e.*, with metallic zinc and dilute sulphuric acid—in a flask arranged as the one spoken of above, and shown in Fig. 37.

FIG. 37.



Flask for dissolving iron for volumetric determination.

A very much quicker reduction of the ferric into a ferrous compound may be accomplished by adding very slowly with constant stirring a saturated solution of sodium sulphite to the boiling, acidified iron solution contained in the flask until the liquid becomes colorless. All excess of sulphur dioxide is expelled before titrating, by boiling the solution (which should contain a sufficient quantity of hydrochloric acid to decompose all sodium sulphite) for about ten minutes in a flask, arranged as the one mentioned above.

One c.c. of deci-normal potassium permanganate, containing of this salt 0.0031534 gramme, is the equivalent of:

	Gramme.
Amyl nitrite, $C_5H_{11}NO_2$	0.003153
Barium dioxide, BaO_2	0.058390
Calcium hypophosphite, $Ca(PH_2O_2)_2$	0.002121
Ethyl nitrite, $C_2H_5NO_2$	0.037435
Ferric hypophosphite, $Fe_2(PH_2O_2)_6$	0.002088
Ferrous ammonium sulphate, $Fe(NH_4)_2(SO_4)_2.6H_2O$	0.039130
Ferrous carbonate, $FeCO_3$	0.011573
Ferrous oxide, FeO	0.007195
Ferrous sulphate, $FeSO_4$	0.015170
Ferrous sulphate, crystallized, $FeSO_4.7H_2O$	0.027742
Hydrogen dioxide, H_2O_2 (see explanation, page 84)	0.001696
Hypophosphorous acid, HPH_2O_2	0.001647
Iron, in ferrous compounds, Fe	0.005588
Oxalic acid, crystallized, $H_2C_2O_4.2H_2O$	0.006285
Oxygen, O	0.000798
Potassium hypophosphite, KPH_2O_2	0.002598
Potassium nitrite, KNO_2	0.042480
Sodium hypophosphite, $NaPH_2O_2.H_2O$	0.002646
Sodium nitrite, $NaNO_2$	0.034465

Potassium dichromate, $K_2Cr_2O_7 = 293.78$. Whenever this salt acts in the presence of free acid, as an oxidizing agent, it transfers 3 atoms of oxygen upon the deoxidizing agent, thus:

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3[Fe_2(SO_4)_3].$$

A normal solution should, therefore, contain one-sixth of the molecular weight, or 48.963 grammes per liter. For most purposes a deci-normal solution is preferred, and this is made by dissolving 4.8963 grammes of pure potassium dichromate in a sufficient quantity of water to make 1000 c.c.

The disadvantage of this solution is, that the final point of titration cannot be well seen, for which reason, in the determination of iron, for which it is chiefly used, the end of the reaction is determined by the method of spotting, *i. e.*, by taking out a drop of the solution and testing it on a white porcelain plate with a drop of freshly prepared potassium ferricyanide solution; when this no longer gives a blue color, the reaction is at an end.

In all determinations by this solution dilute sulphuric acid has to be added, because both the potassium and chromium require an acid to combine with, as shown in the above equation.

The titration equivalents of this solution for ferrous salts are the same as those of deci-normal potassium permanganate solution.

Iodimetry. Solutions of iodine and of sodium thiosulphate (hyposulphite) act upon one another with the formation of sodium iodide and sodium tetrathionate:

$$2I + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6.$$

A normal solution of one can be standardized by a normal solution of the other. As indicator is used starch solution, which is colored blue by minute portions of free iodine.

Starch solution is made by mixing 1 gramme of starch with 10 c.c. of cold water, and then adding enough boiling water, under constant stirring, to make about 200 c.c. of a transparent jelly. If the solution is to be preserved for any length of time, 10 grammes of zinc chloride should be added.

Many other substances, such as sulphurous acid, hydrogen sulphide, arsenous oxide, act upon iodine with the formation of colorless compounds, and may, therefore, be estimated by normal solution of iodine, while the iodine may be standardized by the thiosulphate solution. In many cases the latter solution is also used for the determination of chlorine, which is caused to act upon potassium iodide, the liberated iodine being titrated.

Deci-normal iodine solution is the one generally used, and is made by dissolving 12.653 grammes of pure iodine in a solution of 18 grammes of potassium iodide in about 300 c.c. of water, diluting the solution to 1000 c.c.

To the article to be estimated by this solution is added a little starch solution, and then the iodine solution until, on stirring, the blue color ceases to be discharged.

Many substances, such as sulphurous acid and its salts, hydrogen sulphide, arsenous oxide, etc., are acted upon by iodine in such a manner that this element enters into combination with constituents of the compounds named. The quantity of iodine thus taken up forms the basis for calculating the quantity of the substance acted upon.

In the case of *arsenous oxide* the titration is made in alkaline solution. Arsenous oxide and sodium bicarbonate are dissolved in water, and this solution, containing sodium met-arsenite, is titrated with iodine solution, when sodium met-arsenate and sodium iodide are formed:

$$NaAsO_2 + 2I + 2NaHCO_3 = NaAsO_3 + 2NaI + H_2O + 2CO_2.$$

When *sulphurous acid*, *sulphites*, or *acid sulphites* are titrated with iodine the addition of an alkali is unnecessary; the action is this:

$$\begin{aligned} H_2S + 2I &= 2HI + S. \\ H_2SO_3 + 2I + H_2O &= H_2SO_4 + 2HI. \\ Na_2SO_3 + 2I + H_2O &= Na_2SO_4 + 2HI. \end{aligned}$$

In the titration of *antimony and potassium tartrate* by iodine an alkaline solution is required, and for this reason sodium bicarbonate is added to the solution. The reaction which takes place is somewhat doubtful, but the following equation, even if not absolutely correct, corresponds to the quantities of the substances acting upon one another:

$$\begin{aligned} &2KSbOC_4H_4O_6 + H_2O + 4I + 4NaHCO_3 = \\ &2HSbO_3 + 2KHC_4H_4O_6 + 4NaI + 4CO_2 + H_2O. \end{aligned}$$

One c.c. of deci-normal iodine solution, containing of iodine 0.012653 gramme, is the equivalent of:

	Gramme.
Antimony and potassium tartrate, $2KSbOC_4H_4O_6.H_2O$	0.016560
Arsenous oxide, As_2O_3	0.004942
Hydrogen sulphide, H_2S	0.001699
Potassium sulphite, crystallized, $K_2SO_3.2H_2O$	0.009692
Sodium bisulphite, $NaHSO_3$	0.005193
Sodium hyposulphite (thiosulphate), $Na_2S_2O_3.5H_2O$	0.024764
Sodium sulphite, crystallized, $Na_2SO_3.7H_2O$	0.012579
Sulphur dioxide, SO_2	0.003195

Sodium thiosulphate (Hyposulphite). The crystallized salt, $Na_2S_2O_3.5H_2O = 247.64$, is used for making the deci-normal solution by dissolving 24.764 grammes of the pure crystallized salt in water to make 1000 c.c. If the salt should not be absolutely pure, a somewhat larger quantity (30 grammes) should be dissolved in 1000 c.c. of water, and this solution titrated with deci-normal solution of iodine and diluted with a sufficient quantity of water to obtain the deci-normal solution.

The article to be tested, containing free iodine, either in itself or after the addition of potassium iodide, is treated with this solution until the color of iodine is nearly discharged, when a little starch liquor is added, and the addition of the solution continued until the blue color has just disappeared.

The titration of iron in ferric salts by hyposulphite is based on the liberation of iodine from potassium iodide by all ferric salts:

$$Fe_2Cl_6 + 2KI = 2FeCl_2 + 2KCl + 2I.$$

The reaction shown in the above equation requires a temperature of 40° to 50° C. (104° to 122° F.), and at least half an hour's time to make sure of its completion. The digestion should be performed in a closed flask. If iron be present in combination with organic acids, the addition of some hydrochloric acid becomes necessary. Before titration the solution is allowed to cool, and the titration should be promptly finished, as otherwise errors by re-oxidation of the ferrous salt may be made.

One c.c. of deci-normal solution of sodium thiosulphate, containing of the crystallized salt 0.024764 gramme, is the equivalent of:

	Gramme.
Bromine, Br	0.007976
Chlorine, Cl	0.003537
Iodine, I	0.012653
Iron, Fe, in ferric salts	0.005588

Deci-normal bromine solution (*Koppeschaar's solution*). The great volatility of bromine, even from aqueous solutions, interferes very much with the stability of volumetric solutions. For this reason a solution is prepared which does not contain free bromine, but an alkali bromide and bromate, from which, by addition of an acid, a definite quantity of bromine (7.976 grammes per liter) may be liberated when required. The chemical change is this:

$$5NaBr + NaBrO_3 + 6HCl = 6NaCl + 3H_2O + 6Br.$$

As the bromine salts are rarely chemically pure, a solution is made which is stronger than necessary and is then adjusted to the titer of hyposulphite solution.

The solution is prepared as follows: Dissolve 3 grammes of sodium bromate, and 50 grammes of sodium bromide (or 3.2 and 50 grammes of the potassium salts) in 900 c.c. of water. Of this solution, which is too concentrated, transfer 20 c.c. into a bottle of about 250 c.c. provided with a glass stopper. Next add 75 c.c. of water, 5 c.c. of pure hydrochloric acid, and immediately insert the stopper. Shake the bottle a few times to cause the liberation of bromine, then quickly introduce 1 gramme of potassium iodide, taking care that no bromine vapor escape. Gradually an equivalent quantity of iodine is liberated from the potassium iodide by the bromine. When this has taken place add to the contents of the flask a little starch solution and from a burette deci-normal hyposulphite solution until the blue color has been discharged.

The use of bromine solution is directed by the U. S. P. in one case only, viz., for the volumetric determination of phenol (carbolic acid). This substance forms with bromine tribromphenol and hydrobromic acid:

$$C_6H_5OH + 6Br = C_6H_2Br_3OH + 3HBr.$$

The molecular weight of phenol is 93.78, and as it reacts with 6 atoms of bromine, one-sixth of 93.78, or 15.63 grammes of phenol correspond to one liter of normal, and 1.563 grammes of deci-normal bromine solution; *i. e.*, 1 c.c. of deci-normal bromine solution corresponds to 0.001563 gramme of phenol. The U. S. P. directs the assay to be made as follows: Dissolve 1.563 gramme of the specimen in water to make 1 liter. Transfer 25 c.c. of this solution (0.0391 phenol) to a glass stoppered bottle of about 200 c.c. capacity, and add 30 c.c. of deci-normal bromine solution and 5 c.c. of hydrochloric acid. Shake the contents of the bottle repeatedly, during half an hour, then quickly introduce 1 gramme of potassium iodide, allow the reaction to take place and titrate the solution with deci-normal hyposulphite, as described above. Deduct the number of c.c. of hyposulphite used from the 30 c.c. of bromine solution. The remainder multiplied by 4 indicates the percentage of phenol in the carbolic acid examined.

Deci-normal solution of silver. The pure, dry crystallized silver nitrate, $AgNO_3 = 169.55$, is used for this solution, which is made by dissolving 16.955 grammes of the salt in water to make 1000 c.c. The standard of this solution may be found by means of a deci-normal solution of sodium chloride containing of this salt 5.837 grammes in one liter.

Volumetric silver solution is used directly for the estimation of most chlorides, iodides, bromides, and cyanides, including the free acids of these salts. Insoluble chlorides must first be converted into a soluble form by fusing them with sodium hydroxide, dissolving the fused mass (containing sodium chloride) in water, filtering and neutralizing with nitric acid.

The hydroxides and carbonates of alkali metals and of alkaline earths may be converted into chlorides by evaporation to dryness with pure hydrochloric acid, and heating to about 120° C. (248° F.). The chlorides thus obtained may be titrated with silver solution.

In the case of chlorides, iodides, and bromides, normal potassium chromate is used as an indicator. This salt forms with silver nitrate a red precipitate of silver chromate, but not before the silver chloride (bromide or iodide) has been precipitated entirely. In case free acids are determined by silver, these are neutralized with sodium hydroxide before titration.

The operation is conducted as follows: The weighed quantity of the chloride is dissolved in 50–100 c.c. of water, neutralized if necessary, mixed with a little potassium chromate, and silver solution added from the burette until a red coloration is just produced, which does not disappear on shaking.

In estimating cyanides, the operation can be conducted as above described, or it can be modified, use being made of the formation of soluble double cyanides of silver and an alkali metal. The reaction takes place thus:

$$2KCN + AgNO_3 = AgK(CN)_2 + KNO_3.$$

If to this soluble double compound more silver nitrate be added, it is decomposed with the formation of a precipitate of silver cyanide:

$$AgK(CN)_2 + AgNO_3 = 2AgCN + KNO_3.$$

The estimation of hydrocyanic acid or of simple cyanides, according to this method, is accomplished by first rendering slightly alkaline the solution of the substance to be examined by the addition of sodium hydroxide, and then adding the silver solution until a permanent cloudiness is produced in the liquid, which shows that all cyanogen present has been converted into the soluble double salt. As but one-half of the silver solution has been added which is needed for the complete conversion of the cyanogen present into silver cyanide, the number of c.c. of the standard silver solution employed will indicate exactly one-half of the equivalent amount of cyanide present in the solution.

One c.c. of deci-normal silver nitrate solution, containing 0.016955 gramme of $AgNO_3$, is the equivalent of:

	Gramme.
Ammonium bromide, NH_4Br	0.009777
Ammonium chloride, NH_4Cl	0.005338
Ammonium iodide, NH_4I	0.014454
Calcium bromide, $CaBr_2$	0.009971
Ferrous bromide, $FeBr_2$	0.010770
Ferrous iodide, FeI_2	0.015447
Hydriodic acid, HI	0.012753
Hydrobromic acid, HBr	0.008076

	Gramme.
Hydrochloric acid, HCl	0.003637
Hydrocyanic acid, HCN, to first formation of precipitate	0.005396
Hydrocyanic acid, HCN, with indicator	0.002698
Lithium bromide, $LiBr$	0.008677
Potassium bromide, KBr	0.011879
Potassium chloride, KCl	0.007440
Potassium cyanide, KCN, to first formation of precipitate	0.013002
Potassium cyanide, KCN, with indicator	0.006501
Potassium iodide, KI	0.016556
Potassium sulphocyanate, $KCNS$	0.009699
Sodium bromide, $NaBr$	0.010276
Sodium chloride, $NaCl$	0.005837
Sodium iodide, NaI	0.014953
Zinc bromide, $ZnBr_2$	0.011231
Zinc chloride, $ZnCl_2$	0.006792
Zinc iodide, ZnI_2	0.015908

Deci-normal solution of sodium chloride is made by dissolving 5.837 grammes of pure sodium chloride in enough water to make 1000 c.c. The titration is made in neutral solution, normal potassium chromate being used as an indicator. (See explanation in previous paragraph on silver solution.)

One c.c. of deci-normal sodium chloride solution, containing 0.005837 gramme of NaCl, is the equivalent of:

	Gramme
Silver, Ag	0.010766
Silver nitrate, $AgNO_3$	0.016955
Silver oxide, Ag_2O	0.011564

Deci-normal solution of potassium sulphocyanate (*Volhard's solution*). This solution, like the sodium chloride solution, is used as a companion to silver nitrate; it has the advantage that it can be used in acid solutions, with ferric ammonium sulphate (ferric alum) as indicator. Silver nitrate forms in the potassium sulphocyanate a white precipitate of silver sulphocyanate:

$$KCNS + AgNO_3 = AgCNS + KNO_3.$$

As indicator is used ferric alum, which produces with sulphocyanate a deep brownish-red color, which, however, does not appear permanently until all silver has been precipitated.

As potassium sulphocyanate is rarely pure, 10 grammes, which is about 3 per cent. more than the quantity required, are dissolved in 1000 c.c. of water. This solution has to be adjusted by standardizing with deci-normal silver solution until equal volumes decompose one another exactly.

The sulphocyanate solution is used in the determination of the amount of ferrous iodide in the saccharated salt and in the syrup.

The operation is performed thus: To the solution of the ferrous iodide are added nitric acid, ferric alum, and of deci-normal silver nitrate solution a quantity more than sufficient to convert all iodine into silver iodide. The excess of silver nitrate present in the mixture is determined by sulphocyanate solution.

The titration equivalents of this solution for silver are the same as those of deci-normal sodium chloride.

Gas-analysis. The analysis of gases is generally accomplished by measuring gas volumes in graduated glass tubes (eudiometers) over mercury (in some cases over water), noting carefully the pressure and temperature at which the volume is determined.

From gas mixtures, the various constituents present may often be eliminated by causing them to be absorbed one after another by suitable agents. For instance: From a measured volume of a mixture of nitrogen, oxygen, and carbon dioxide, the latter compound may be removed by allowing the gas to remain in contact for a few hours with potassium hydroxide, which will absorb all carbon dioxide, the diminution in volume indicating the quantity of carbon dioxide originally present. The volume of oxygen may next be determined by introducing a piece of phosphorus, which will gradually absorb the oxygen, the remaining volume being pure nitrogen.

In some cases gaseous constituents of liquids or solids are eliminated and measured as gases. Thus, the carbon dioxide of carbonates, the nitrogen dioxide evolved from nitrates, the nitrogen of urea and other nitrogenous bodies, are instances of substances which are eliminated from solids in the gaseous state and determined by direct measurement.

The gas volume thus found is, in most cases, converted into parts by weight. The basis of this calculation is the weight of 1 c.c. of hydrogen, which, at the temperature of 0° C. (32° F.) and a pressure of 760 mm., is 0.0000896 gramme. 1 c.c. of any other gas weighs as many more times as the molecule of this substance is heavier than that of hydrogen. Thus the molecular weight of carbon dioxide is 22 times greater than that of hydrogen, consequently 1 c.c. of carbon dioxide weighs 22 times heavier than 1 c.c. of hydrogen, or 0.0019712 gramme.

It has been shown on pages 21 and 25 that heat and pressure cause a regular increase or decrease in volume. The data there given are used in calculating the volume of the measured gas for the temperature of 0° C. (32° F.) and a pressure of 760 m.m.

Methods of gas-analysis have been adopted by the U. S. P. in the quantitative determination of amyl nitrite and ethyl nitrite. The operation is performed in an apparatus known as a nitrometer, consisting of two glass tubes held in upright position and connected at the lower ends by a piece of rubber tubing. One of the tubes is open, the other one is graduated and provided with a glass stopcock near the upper end. In using the nitrometer for the analysis of ethyl nitrite the graduated tube is filled with saturated solution of sodium chloride, in which nitrogen dioxide is almost insoluble. Next are introduced through the stopcock the measured (or weighed) quantity of ethyl nitrite with a sufficient amount of solution of potassium iodide and sulphuric acid. By the action of these agents nitrogen dioxide is liberated, and from the volume obtained the quantity of nitrite present is calculated. The decomposition is shown by the equation:

$$C_2H_5NO_2 + KI + H_2SO_4 = C_2H_5OH + I + KHSO_4 + NO.$$

37. DETECTION OF IMPURITIES IN OFFICIAL INORGANIC CHEMICAL PREPARATIONS.

General remarks. Very little has been said, heretofore, about impurities which may be present in the various chemical preparations, and this omission has been intentional, because it would have increased the bulk of this book beyond the limits considered necessary for the beginner.

Impurities present in chemical preparations are either derived from the materials used in their manufacture, or they have been intentionally added as adulterations. In regard to the last, no general rule for detecting them can be given, the nature of the adulterating article varying with the nature of the substance adulterated; the general

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QUESTIONS.—351. Explain the principles which are made use of in gravimetric and volumetric determinations. 352. Give an outline of the operations to be performed in the gravimetric determination of copper in cupric sulphate. 353. What are normal and deci-normal solutions, and how are they made? 354. What is the use of indicators in volumetric analysis? Mention some indicators and explain their action. 355. Why is oxalic acid preferred in preparing normal acid solution? What quantity of oxalic acid is contained in a liter, and why is this quantity used? 356. Suppose 2 grammes of crystallized sodium carbonate require 14 c.c. of normal acid for neutralization: What are the percentages of crystallized sodium carbonate and of pure sodium carbonate contained in the specimen examined? 357. Ten grammes of dilute hydrochloric acid require 35.5 c.c. of normal sodium hydroxide solution for neutralization. What is the strength of this acid? 358. Explain the action of potassium permanganate and of potassium dichromate when used for volumetric purposes. 359. Which substances may be determined volumetrically by solutions of iodine and sodium thiosulphate? Explain the mode in which the determinations by these agents are accomplished. 360. Suppose 1 gramme of potassium iodide requires for titration 60 c.c. of deci-normal solution of silver nitrate: What quantity of pure potassium iodide is indicated by this determination? 361. Describe in detail the volumetric determination of carbolic acid. 362. For what purposes is potassium sulphocyanate used volumetrically, and what is its action? 363. Explain the method used for the analysis of ethyl nitrite.

properties of the substance to be examined for purity will, in most cases, suggest the nature of those substances which possibly may have been added, and for them a search has to be made, or, if necessary, a complete analysis, by which is proved the absence of everything else but the constituents of the pure substance.

Impurities derived from the materials used in the manufacture of a substance (generally through an imperfect or incorrect process of manufacture), or from the vessels used in the manufacture, are usually but few in number (in any one substance), and their nature can, in most cases, be anticipated by one familiar with the process of manufacture. For one not acquainted with the mode of preparation it would be a rather difficult task to study the nature of the impurities which might possibly be present.

The same remarks apply to the methods by which the impurities can be detected. One familiar with analytical chemistry can easily find, in most cases, a good method by which the presence or absence of an impurity can be demonstrated; but to one unacquainted with chemistry it might be an impossibility to detect impurities, even if a method were given.

For these reasons little stress has been laid upon the occurrence of impurities in the various chemical preparations heretofore considered. Moreover, the U. S. P. gives, in most cases, directions for the detection of impurities, so explicit that anyone acquainted with analytical operations will find no difficulty in performing these tests satisfactorily.

However, while the Pharmacopœia gives exact instructions how to manipulate, it furnishes no explanations why certain methods have been adopted, or why certain operations are to be performed. It is for this reason, and for the special benefit of the beginner, that a few paragraphs are devoted to the consideration of official methods for testing the chemical preparations of the U. S. P.

Official chemicals and their purity. Absolute purity of chemicals is essential in some cases, as, for instance, when they are intended as reagents; such chemicals are commercially designated as C. P. (chemically pure). For the majority of medicinal chemicals, however, such absolute purity is unnecessary, as the small proportion of harmless impurities present in no wise interferes with the therapeutic action of the substance, and a demand for absolute purity, which greatly enhances the cost of chemicals, is therefore unreasonable and not required by the Pharmacopœia.

The presence of a small fraction of one per cent. of sodium chloride in many official chemicals cannot be looked upon as objectionable, while the same amount of arsenic would render the preparation unfit for medicinal use.

The methods used by the Pharmacopœia to determine the quality of a chemical preparation may be divided into four classes, as follows: 1. Tests as to identity; 2. Qualitative tests for impurities; 3. Quantitative tests for the limit of impurities; 4. Quantitative determination of the chief constituent.

Tests as to identity. These tests are partly of a physical, partly of a chemical character. They include, in the physical part, the examination of the appearance, color, crystalline structure, specific gravity, fusing-point, boiling-point, etc.

The chemical tests given are sufficiently characteristic to leave no doubt as to the true nature or identity of the substance. In order to accomplish this object it is not necessary to apply *all* the analytical reagents characteristic of the substance or its component parts, but the U. S. P. selects from the often large number of known tests one, or possibly a few, which answer best in the special case.

For instance, while we have a number of tests, both for potassium and iodine, the U. S. P., in the article on potassium iodide, gives but one reaction for each of these elements. Yet these tests have been selected with sufficient judgment to admit of no doubt regarding the nature of the substance.

Qualitative tests for impurities. These tests are in many cases described minutely, *i. e.*, the quantity to be taken of both the substance to be examined and the reagent to be added is stated. Moreover the amount of solvent (water, acid, etc.) to be used is mentioned, and other details are given. The object of this exactness in describing the tests is not only to render the work easy for one not fully familiar with analytical methods, but also, in some cases, to fix a limit for the admissible quantity of an impurity. A certain reagent may, in a concentrated solution, indicate the presence of a trace of an impurity, while in a more dilute solution this reagent will fail to detect it. The selection of the reagents used in certain tests is also made with the view of establishing a sufficient purity for pharmacopœial purposes of the article examined without demanding an absolute purity.

A few instances may help to illustrate these remarks: Potassium can be precipitated from a solution of its salts by a number of reagents, which, however, differ widely in sensitiveness. Thus, tartaric acid will cause the formation of a precipitate of potassium bitartrate in a solution containing at least 0.1 per cent. of potassium; in solutions containing a less amount no precipitate is formed. Platinic chloride is somewhat more sensitive than tartaric acid, and sodium cobaltic nitrite, which is still more delicate, causes a precipitate in solutions containing even as little as 0.04 per cent. of potassium. It is evident that by using either one or the other of the three reagents mentioned for the detection of potassium, this metal may or may not be found, according to the quantity present in a solution. The Pharmacopœia, in directing the use of one of these reagents, limits the amount of a permissible quantity of potassium according to the sensitiveness of the reagent.

Again, in testing for arsenic, the chemist has his choice between a number of more or less delicate tests. Gutzeit's test is so sensitive that by means of it arsenic can be detected in a solution containing only 0.000001 gramme of arsenous oxide in a cubic centimeter. This test would be, therefore, by far too severe when applied to a number of pharmaceutical preparations, for which reason the Pharmacopœia directs in many cases the less sensitive tests of Bettendorff or Fleitmann.

Quantitative tests for the limit of impurities. While, as above stated, even the qualitative tests are often so made as to be to some extent of a quantitative character, the U. S. P. recommends in many cases methods by which a stated limit of an impurity can be detected without the necessity of determining by quantitative analysis the actual amount of the impurity present.

Formerly it was, and to some extent it is now, customary to limit the amount of a permissible quantity of an impurity by referring to the intensity of the reaction. In case the impurity was to be detected by precipitation (as, for instance, sulphates or chlorides in potassium nitrate) it was stated that the respective reagents used for the detection (in the case named, barium chloride or silver nitrate) should not produce more than a very slight precipitate, or turbidity, or cloudiness, etc. These descriptions are, of course, very indefinite, and the conclusion arrived at depends largely upon the individuality of the observer.

In order to obviate this uncertainty the U. S. P. has introduced a number of more exact methods. These depend upon the addition of a definite quantity of a reagent capable of eliminating a certain quantity of the impurity from a given quantity of the substance to be examined. In thus examining a preparation the impurity may or may not be present; if present, the permissible quantity will be removed by the operation, and if originally not present in larger quantity, the substance will now be found free from the impurity, while if present in larger proportions than can be removed by the quantity of reagent added, the excess can be detected by appropriate tests.

If an excess of impurity is thus discovered, regardless of the fact whether the excess be large or small, the substance examined does not come up to the pharmacopœial requirements.

For instance, the Pharmacopœia fixes the limit of potassium chloride in potassium carbonate at 0.15 per cent., and in order to determine whether this limit is exceeded or not the Pharmacopœia directs the addition of 0.1 c.c. of deci-normal silver nitrate solution to a solution of 0 5 gramme of potassium carbonate in 6 c.c. of diluted nitric acid and 4 c.c. of water. After removing the precipitated silver chloride by filtration no precipitate should be produced in the filtrate by the further addition of silver nitrate solution. The limit of many impurities, which can be separated by precipitation in definite quantity, is thus determined.

In other cases the limited quantity of an impurity may be determined without the formation of a precipitate, as, for instance, an alkaline impurity in an otherwise neutral salt by the addition of a standard acid.

Thus, in potassium bromide, the pharmacopœial limit of potassium carbonate is 1.38 per cent. In order to determine whether or not this limit is exceeded, the Pharmacopœia directs the addition of 0.2 c.c. of normal sulphuric acid to a solution of 1 gramme of the salt in 100 c.c. of water. Since 0.1 c.c. of normal sulphuric acid is capable of neutralizing 0.0069 gramme of potassium carbonate, the whole quantity allowed, 1.38 per cent. or 0.0138 gramme, would be neutralized by the addition of the prescribed quantity of acid, and no red tint should be imparted to the liquid by adding a few drops of phenol-phtalein solution ; a red color would indicate that more alkali carbonate was present in the weighed sample than could be neutralized by the quantity of acid added.

By methods similar to those described, the limit of many other impurities is determined, as, for instance, the limit of sulphuric acid by removing it with barium chloride, or that of carbonates in caustic alkalies by lime-water.

Quantitative determination of the principal constituent. These determinations are made in the majority of cases volumetrically, and require no special explanation here, as the methods have been fully considered in the previous chapter. Gravimetric methods are used in the determination of the alkaloids of cinchona and opium, and also in a few other cases.

QUESTIONS.—364. What are the sources of the impurities found in chemical preparations? 365. Why is it not obligatory to use chemically pure chemicals for medicinal purposes? 366. Which are the leading features adopted by the U. S. P. in the identification of chemical preparations? 367. State the reasons why the U. S. P. describes the tests for impurities so minutely. 368. Why can we not use indiscriminately either one of a number of reagents or tests by which the presence of the same impurity may be indicated? 369. What is the principle applied in the methods of the Pharmacopœia for the determination of a permitted quantity of an impurity? 370. How can we decide the question whether a sample of potassium acetate contains more than 1 per cent. of potassium chloride without making a quantitative estimation of chlorine?

VI.

CONSIDERATION OF CARBON COMPOUNDS, OR ORGANIC CHEMISTRY.

38. INTRODUCTORY REMARKS. ELEMENTARY ANALYSIS.

Definition of organic chemistry. The term *organic chemistry* was originally applied to the consideration of compounds formed in plants and in the bodies of animals, and these compounds were believed to be created by a mysterious power, called "vital force," supposed to reside in the living organism.

This assumption was partly justified by the failure of the earlier attempts to produce these compounds by artificial means, and also by the fact that the peculiar character of the compounds, and the numerous changes which they constantly undergo in nature, could not be sufficiently explained by the experimental methods then known, and the laws then established.

It was in accordance with these views that a strict distinction was made between inorganic and organic compounds, and accordingly between inorganic and organic chemistry, the latter branch of the science considering the substances formed in the living organism and those compounds which were produced by their decomposition.

Since that time it has been shown that many substances which formerly were believed to be exclusively produced in the living organism, under the influence of the so-called vital force, can be formed artificially from inorganic matter, or by direct combination of the elements. It was in consequence of this fact that the theory of the supposed "vital force," by which organic substances could be formed exclusively, had to be abandoned.

An organic compound, according to modern views, is simply a compound of carbon generally containing hydrogen, frequently also oxygen and nitrogen, and sometimes other elements.

Organic chemistry may consequently be defined as the chemistry of carbon compounds. The old familiar terms, organic compounds and organic chemistry, are, however, still in general use.

In a strictly systematically arranged text-book of chemistry organic compounds should be considered in connection with the element carbon itself, but as these carbon compounds are so numerous, their composition often so complicated, and the decompositions which they suffer under the influence of heat or other agents so varied, it has been found best for purposes of instruction to defer the consideration of these compounds until the other elements and their combinations have been studied.

Elements entering into organic compounds. Organic compounds contain generally but a small number of elements. These are, besides carbon, chiefly hydrogen, oxygen, and nitrogen, and sometimes sulphur and phosphorus. Other elements, however, enter occasionally into organic compounds, and by artificial means all metallic and non-metallic elements may be made to enter into organic combinations.

Here the question presents itself: Why is it that the four elements carbon, hydrogen, oxygen, and nitrogen are capable of producing such an immense number (in fact, millions) of different combinations? To this question but one answer can be given, which is that these four elements differ more widely from each other, in their chemical and physical properties, than perhaps any other four elements.

Carbon is a black, solid substance, which has never yet been fused or volatilized, while hydrogen, oxygen, and nitrogen are colorless gases which can only be converted into liquids with difficulty. Moreover, hydrogen is very combustible, oxygen is a supporter of combustion, whilst nitrogen is perfectly indifferent. Finally, hydrogen is univalent, oxygen bivalent, nitrogen trivalent, and carbon quadrivalent. These elements are, therefore, capable of forming a greater number and a greater variety of compounds than would be the case if they were elements of equal valence and of similar properties.

It will be shown later that carbon atoms have, to a higher degree than the atoms of any other element, the power of combining with one another by means of a portion of the affinities possessed by each atom, thus increasing the possibilities of the formation of complex compounds.

General properties of organic compounds. The substances formed by the union of the four elements just mentioned have properties in some respects intermediate to those of their components.

Thus, no organic substance is either permanently solid[1] like carbon, nor an almost permanent gas like hydrogen, oxygen, and nitrogen.

Some organic substances are solids, others liquids, others gases; they are generally solids when the carbon atoms predominate; they are liquids or gases when the gaseous elements, and especially hydrogen, predominate; likewise, it may also be said that compounds containing a small number of atoms in the molecule are gases or liquids which are easily volatilized; they are liquids of high boiling-points, or solids, when the number of atoms forming the molecules is large.

The combustible property of carbon and hydrogen is transferred to all organic substances, every one of which will burn when sufficiently heated in atmospheric air. (If carbon dioxide, carbonic acid and its salts be considered organic compounds, we have an exception to the rule, as they are not combustible.)

The properties possessed by organic compounds are many and widely different. There are organic acids, organic bases, and organic neutral substances; there are some organic compounds which are perfectly colorless, tasteless, and odorless, whilst others show every possible variety of color, taste, and odor; many serve as food, whilst others are most poisonous; in short, organic substances show a greater variety of properties than the combinations formed by any other four elements.

And yet, the cause of all the boundless variety of organic matter is that peculiar attraction called chemical affinity, acting between the atoms of a comparatively small number of elements and uniting them in many thousand different proportions.

It would, of course, be entirely inconsistent with the object of this book, if all the thousands of organic substances already known (the number of which is continually being increased by new discoveries) were to be considered, or even mentioned. It must be sufficient to state the general properties of the various groups of organic substances, to show by what processes they are produced artificially or how they are found in nature, how they may be recognized and separated, and, finally, to point out those members of each group which claim a special attention for one reason or another.

Difference in the analysis of organic and inorganic substances. The analysis of organic substances differs from that of inorganic substances, in so far as the qualitative examination of an organic substance furnishes in many cases but little proof of the true nature of the substance (except that it is organic), whilst the qualitative analysis of an inorganic substance discloses in most cases the true nature of the substance at once.

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[1] Non-volatile organic substances are decomposed by heat with generation of volatile products.

For instance: If a white, solid substance, upon examination, be found to contain potassium and iodine, and nothing else, the conclusion may at once be drawn that the compound is potassium iodide, containing 39 parts by weight of potassium, and 126.5 parts by weight of iodine. Or, if another substance be examined, and found to be composed of mercury and chlorine, the conclusion may be drawn that the compound is either mercurous or mercuric chloride, as no other compounds containing these two elements are known, and whether the examined substance be the lower or higher chloride of mercury, or a mixture of both, can easily be determined by a few simple tests.

Whilst thus the qualitative examination discloses the nature of the substance, it is different with organic compounds. Many thousand times the analysis might show carbon, hydrogen, and oxygen to be present, and yet every one of the compounds examined might be entirely different; it is consequently not only the *quality* of the elements, but chiefly the *quantity* present which determines the nature of an organic substance, and in order to identify an organic substance with certainty, it frequently becomes necessary to make a quantitative determination of the various elements present, and this quantitative analysis by which the elements in organic substances are determined is generally called *ultimate or elementary analysis.*

There are, however, for many organic substances such characteristic tests that these substances may be recognized by them; these reactions will be mentioned in the proper places.

An analysis by which different organic substances, when mixed together, are separated from each other is frequently termed *proximate analysis.* Such an analysis includes the separation and determination of essential oils, fats, alcohols, sugars, resins, organic acids, albuminous substances, etc., and is one of the most difficult branches of analytical chemistry.

Qualitative analysis of organic substances. The presence of *carbon* in a combustible form is decisive in regard to the organic nature of a compound. If, consequently, a substance burns with generation of carbon dioxide (which may be identified by passing the gas through lime-water), the organic nature of this substance is established.

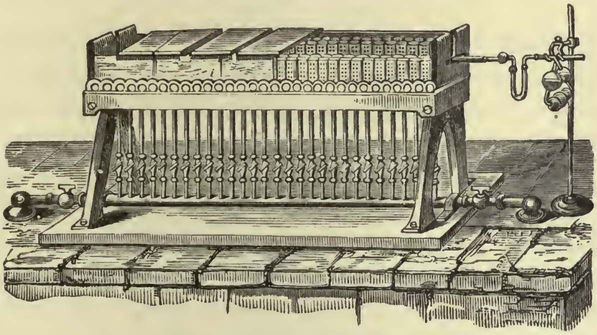
The presence of *hydrogen* can be proven by allowing the gaseous products of the combustion to pass through a cool glass tube, when drops of water will be deposited.

It is difficult to show by qualitative analysis the presence or absence of *oxygen* in an organic compound, and its determination is therefore generally omitted.

The presence of *nitrogen* is determined by heating the substance with dry *soda-lime* (a mixture of two parts of calcium hydroxide and one part of sodium hydroxide), when the nitrogen is converted into ammonia gas, which may be recognized by its odor or by its action on paper moistened with solution of cupric sulphate, a dark-blue color indicating ammonia.

Ultimate or elementary analysis. While the student must be referred to books on analytical chemistry for a detailed description of the apparatus required and the methods employed for elementary analysis, it may here be stated that the quantitative determination of carbon and hydrogen is generally accomplished by the following process: A weighed quantity of the pure and dry substance is mixed with a large excess of dry cupric oxide, and this mixture is introduced into a glass tube, the open end of which is connected by means of a perforated cork and tubing with two glass vessels, the first one of which (generally a U-shaped tube) is filled with pieces of calcium chloride, the other (usually a tube provided with several bulbs) with solution of potassium hydroxide. The two glass vessels, containing the substances named, are weighed separately after having been

FIG. 38.



Gas-furnace for organic analysis.

filled. Upon heating the combustion-tube in a suitable furnace, the organic matter is burned by the oxygen of the cupric oxide, the hydrogen is converted into water (steam), which is absorbed by the calcium chloride, and the carbon is converted into carbon dioxide, which is absorbed by the potassium hydroxide. The apparatus represented in Fig. 38 shows the gas-furnace in which rests the combustion-tube with calcium chloride tube and potash bulb attached. Upon re-weighing the two absorbing vessels at the end of the operation, the increase in weight will indicate the quantity of water and carbon dioxide formed during the combustion, and from these figures the amount of carbon and hydrogen present in the organic matter may easily be calculated.

For instance: 0.81 gramme of a substance having been analyzed, furnishes, of carbon dioxide 1.32 gramme, and of water 0.45 gramme. As every 44 parts by weight of carbon dioxide contain 12 parts by weight of carbon, the above 1.32 gramme contains of carbon 0.36 gramme, or 44.444 per cent. As every 18 parts of water contain 2 parts of hydrogen, the above 0.45 gramme consequently contains 0.05 gramme, or 6.172 per cent.

Oxygen is scarcely ever determined directly, but generally indirectly, by determining the quantity of all other elements and deducting their weight, calculated to percentages from 100. The difference is oxygen.

If, in the above instance, 44.444 per cent. of carbon and 6.172 per cent. of hydrogen were found to be present, and all other elements, except oxygen, to be absent, the quantity of oxygen is, then, equal to 49.384 per cent. and the composition of the substance is as follows:

Carbon	44.444	per cent.
Hydrogen	6.172	"
Oxygen	49.384	"
	100 000	

Determination of nitrogen. Nitrogen is generally determined by heating the substance with soda-lime and passing the generated ammonia gas through hydrochloric acid contained in a suitable glass vessel. Upon evaporation of the acid solution in a weighed platinum dish over a water-bath, ammonium chloride is left, from the weight of which compound the quantity of nitrogen may be calculated. Or the ammonia gas may be passed through a measured volume of normal hydrochloric acid and the unsaturated portion of the acid determined volumetrically.

Determination of sulphur and phosphorus. These elements are determined by mixing the organic substance with sodium carbonate and nitrate, and heating the mixture in a crucible. The oxidizing action of the nitrate converts all carbon into carbon dioxide, hydrogen into water, sulphur into sulphuric acid, phosphorus into phosphoric acid. The latter two acids combine with the sodium of the sodium carbonate, forming sulphate and phosphate of sodium. The fused mass is dissolved in water, and sulphuric acid precipitated by barium chloride, phosphoric acid by magnesium sulphate and ammonium hydroxide and chloride. From the weight of barium sulphate and magnesium pyrophosphate the weight of sulphur and phosphorus is calculated.

Determination of atomic composition from results obtained by elementary analysis. The elementary analysis gives the quantity of the various elements present in percentages, and from these figures the relative number of atoms may be found by dividing the figures by the respective atomic weights. For instance: The analysis above mentioned gave the composition of a compound, as carbon 44.444 per cent., hydrogen 6.172 per cent., and oxygen 49.384 per cent. By dividing each quantity by the atomic weight of the respective element, the following results are obtained:

$$\frac{44.444}{12} = 3.703$$

$$\frac{6.172}{1} = 6.172$$

$$\frac{49.384}{16} = 3.087$$

The figures 3.703, 6.172, and 3.087, represent the relative number of atoms present in a molecule of the compound examined. In order to obtain the most simple proportion expressing this relation, the greatest divisor common to the whole has to be found, a task which is sometimes rather difficult on account of slight errors made in the quantitative determination itself. In the above case, 0.6172 is the greatest divisor, which gives the following results:

$$\frac{3.703}{0.6172} = 6; \quad \frac{6.172}{0.6172} = 10; \quad \frac{3.087}{0.6172} = 5.$$

The simplest numbers of atoms are, accordingly, carbon 6, hydrogen 10, oxygen 5, or the composition is $C_6H_{10}O_5$.

Empirical and molecular formulas. A chemical formula is termed *empirical* when it merely gives the simplest possible expression of the composition of a substance. In the above case, the formula $C_6H_{10}O_5$ would be the empirical formula. It might, however, be possible that this formula did not represent the actual number of atoms in the molecule, which might contain, for instance, twice or three times the number of atoms given, in which case the true composition would be expressed by the formula $C_{12}H_{20}O_{10}$ or $C_{18}H_{30}O_{15}$.

If it could be proven that one of the latter formulas is the correct one, it would be termed the *molecular formula,* because it expresses not only the numerical relations existing between the atoms, but also the absolute number of atoms of each element contained in the molecule.

The best method for determining the actual number of atoms contained in the molecule is the determination of the specific weight of the gaseous compound, taking hydrogen as the unit. For instance: Assume the analysis of a liquid substance gave the following result:

Carbon	92.308	per cent.
Hydrogen	7.692	"
	100.000	

From this result the empirical formula, CH, is deducted by applying the method stated above. If this formula were the molecular formula, the density of the vapors of the substance would, when compared with hydrogen (according to the law of Avogadro), be equal to 6.5, because a molecule of hydrogen weighs 2 and a molecule of the compound CH weighs 13.

Suppose, however, the density of the gaseous substance is found to be 39, then the molecular formula would be expressed by C_6H_6, because its molecular weight ($6 \times 12 + 6 \times 1$) is equal to 78, which weight, when compared with the molecular weight of hydrogen $= 2$, gives the proportions 78 : 2, or 39 : 1.

Not all organic compounds can be converted into gases or vapors without undergoing decomposition, and the determination of the molecular formulas of such compounds has to be accomplished by other methods. If the substance, for instance, is an acid or a base, the molecular formula may be determined by the analysis of a salt formed by these substances. For instance: The empirical formula of acetic acid is CH_2O; the analysis of the potassium acetate, however, shows the composition $KC_2H_3O_2$, from which the molecular formula $HC_2H_3O_2$ is deducted for acetic acid.

In many cases, however, it is as yet absolutely impossible to give with certainty the molecular formula of some compounds.

Rational, constitutional, structural, or graphic formulas. These formulas are intended to represent the theories which have been formed in regard to the arrangement of the atoms within the molecule, or to represent the modes of the formation and decomposition of a compound, or the relation which allied compounds bear to one another.

The molecular formula of acetic acid, for instance, is $C_2H_4O_2$, but different constitutional formulas have been used to represent the structure of the acetic acid molecule.

Thus, $H.C_2H_3O_2$ is a formula analogous to $H.NO_3$, indicating that acetic acid (analogous to nitric acid), is a monobasic acid, containing one atom of hydrogen, which can be replaced by metallic atoms.

$C_2H_3O^{i}.OH^{i}$ is a formula indicating that acetic acid is composed of two univalent radicals which may be taken out of the molecule and replaced by other atoms or groups of atoms. This formula indicates also that acetic acid is analogous to hydroxides, the radical C_2H_3O having replaced one atom of hydrogen in H_2O.

$CH_3.CO_2H^{i}$ is a formula indicating that acetic acid is composed of the two compound radicals, methyl and carboxyl.

It may be said finally, that quite a number of other rational formulas have been applied, or, at least, have been proposed by different chemists and at different times, to represent the structure of acetic acid, but it should be remembered that these formulas are not intended to represent the actual arrangement of the atoms in space, but only, as it were, their relative mode of combination, showing which atoms are combined directly and which only indirectly, that is, through the medium of others.

QUESTIONS.—371. What is organic chemistry, according to modern views? 372. Mention the chief four elements entering into organic compounds, and name the elements which may be made to enter into organic compounds by artificial processes. 373. State the reason why the four elements, carbon, hydrogen, oxygen, and nitrogen, are better adapted to form a large number of compounds than most other elements. 374. State the general properties of organic compounds. 375. Why does a qualitative analysis of an organic compound, in most cases, not disclose its true nature? 376. By what test may the organic nature of a compound be established? 377. By what tests may the presence of carbon, hydrogen, and nitrogen be demonstrated in organic compounds? 378. State the methods by which the elements carbon, hydrogen, oxygen, sulphur, and phosphorus are determined quantitatively. 379. By what general method may a formula be deducted from the results of a quantitative analysis? 380. What is meant by an empirical, molecular, and constitutional formula; how are they determined; and what is the difference between them?

39. CONSTITUTION, DECOMPOSITION, AND CLASSIFICATION OF ORGANIC COMPOUNDS.

Radicals or residues. The nature of a radical or residue has been stated already in Chapter 8, but the important part played by radicals in organic compounds renders it necessary to consider them more fully.

A radical is an unsaturated group of atoms obtained by removal of one or more atoms from a saturated compound. It is not necessary that this removal of atoms should be practically accomplished in order to call a group of atoms a radical, but it is sufficient to prove that the unsaturated group of atoms exists as such in a number of compounds, and that it can be transferred from one compound into another without suffering decomposition.

Radicals exist in organic and inorganic compounds; an inorganic radical spoken of heretofore is the water residue or hydroxyl, OH, obtained by removal of one atom of hydrogen from one molecule of water. Hydroxyl does not exist in the separate state, but it exists in hydrogen dioxide, H_2O_2, or HO—OH, and is also a constituent of the various hydroxides, as, for instance, of KOH, $Ca(OH)_2$, $Fe_2(OH)_6$, etc.

If one atom of hydrogen be removed from the saturated hydrocarbon methane, CH_4, the univalent residue methyl, CH_3, is left, which is capable of combining with univalent elements, as in methyl chloride, CH_3Cl, or, with univalent residues, as in methyl hydroxide, CH_3OH.

If two atoms of hydrogen be removed from CH_4, the bivalent residue methylene, CH_2, is left, capable of forming the compounds CH_2Cl_2, $CH_2(OH)_2$, etc.

If three atoms of hydrogen be removed from CH_4, the trivalent residue CH is left, capable of combining with three atoms of univalent elements, as in $CHCl_3$, or with another trivalent radical, etc.

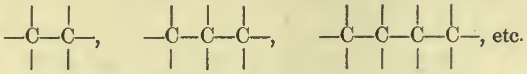
Chains. The expression, chain, designates a series of multivalent atoms (generally, but not necessarily, of the same element), held together in such a manner that affinities are left unsaturated. For instance:

$$—O—O—,\quad —O—O—O—,\quad —O—O—O—O—,$$

are oxygen chains, each one of which has two free affinities which may be saturated, for instance, with the following results:

H—O—O—H,	H—O—O—O—Cl,	H—O—O—O—O—Cl,
Hydrogen peroxide.	Chloric acid.	Perchloric acid.

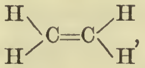
In a similar manner, carbon atoms unite, forming chains, as, for instance :



$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-,\quad -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-,\quad -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-,\text{ etc.}$$

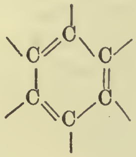
The above carbon chains have 6, 8, and 10 free affinities, respectively, which may be saturated by the greatest variety of atoms or radicals. The chain combination of carbon, above indicated by the first three members of a series, may, as far as is known, be continued indefinitely. This fact, in connection with the possibility of saturating the free affinities with various atoms or radicals, indicates the almost unlimited number of possible combinations to be formed in this way. In fact, the existence of such an enormous number of carbon compounds is greatly due to the property of carbon to form these chains.

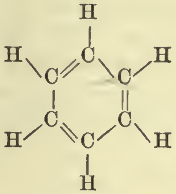
It is not always the case that the atoms when forming a chain are united by one affinity only, as above, but they may be united by two or three affinities, as indicated by the compounds C_2H_4 and C_2H_2, the graphic formulas of which may be represented by



$H-C{\equiv}C-H.$

Finally, it is assumed that the carbon atoms are united partially by double and partially by single union, as, for instance, in the so-called *closed chain* of C_6, capable of forming the saturated hydrocarbon benzene, C_6H_6 :

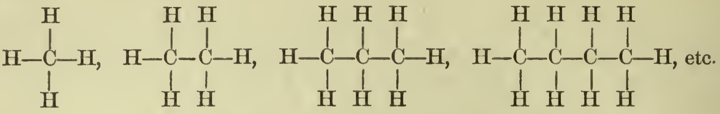




A chain has also been termed a skeleton, because it is that part of an organic compound around which the other elements or radicals arrange themselves, filling up, as it were, the unsaturated affinities.

Homologous series. This term is applied to any series of organic compounds the terms or members of which, preceding or following each other, differ by CH_2. Moreover, the general character, the constitution, and the general properties of the members of an homologous series are similar.

The explanation regarding the formation of an homologous series is to be found in the above-described property of carbon to form chains. By saturating, for instance, the affinities in the open carbon chains mentioned above, we obtain the compounds CH_4, C_2H_6, C_3H_8, C_4H_{10}, etc.

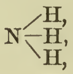
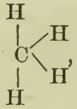
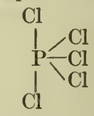


$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H, \\ & | & \\ & H & \end{array} \quad \begin{array}{cccc} & H & H & \\ & | & | & \\ H- & C- & C & -H, \\ & | & | & \\ & H & H & \end{array} \quad \begin{array}{ccccc} & H & H & H & \\ & | & | & | & \\ H- & C- & C- & C & -H, \\ & | & | & | & \\ & H & H & H & \end{array} \quad \begin{array}{cccccc} & H & H & H & H & \\ & | & | & | & | & \\ H- & C- & C- & C- & C & -H, \text{ etc.} \\ & | & | & | & | & \\ & H & H & H & H & \end{array}$$

Many homologous series of various organic compounds are known, as, for instance :

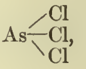
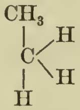
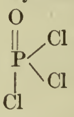
$C H_3 Cl$,	$C H_4 O$,	$C H_2 O_2$.
$C_2H_5 Cl$,	$C_2H_6 O$,	$C_2H_4 O_2$.
$C_3H_7 Cl$,	$C_3H_8 O$,	$C_3H_6 O_2$.
$C_4H_9 Cl$,	$C_4H_{10}O$,	$C_4H_8 O_2$.
$C_5H_{11}Cl$,	$C_5H_{12}O$,	$C_5H_{10}O_2$.
etc.	etc.	etc.

Types. It has been proposed to select some substances in which the arrangement of atoms in the molecules may be taken as representative of whole classes of other substances, the molecules of which have a similar arrangement, and these normal substances have been termed types. Most substances may be classified under the following five types :

I.	II.	III.	IV.	V.
Hydrogen.	Water.	Ammonia.	Methane.	Phosphoric chloride.
H—H,	H—O—H,			

By replacing the constituents of these types by other elements or radicals of equal valence, most of the compounds known (both organic and inorganic) may be classed in one of these types.

The following five substances may, for instance, be said to have an atomic arrangement similar to the types above stated:

I.	II.	III.	IV.	V.
Hydrochloric acid.	Potassium hydroxide.	Arsenous chloride.	Ethane.	Phosphoric oxychloride.
H—Cl,	K—O—H,			

The graphic representation of the constitution of compounds according to types has greatly aided in disclosing their structure, and is frequently used to give a picture, as it were, of the theoretical views held regarding the atomic arrangement.

Substitution is a term used for those reactions or chemical changes which depend on the replacement of an atom or a group of atoms by other atoms or groups of atoms. Substitution takes place in organic or inorganic substances, and its nature may be illustrated by the following instances:

$$\underset{\text{Potassium.}}{K} + \underset{\text{Water.}}{H_2O} = \underset{\text{Potassium hydroxide.}}{KOH} + \underset{\text{Hydrogen.}}{H.}$$

$$\underset{\text{Acetic acid.}}{C_2H_4O_2} + \underset{\text{Chlorine.}}{2Cl} = \underset{\text{Monochloracetic acid.}}{C_2H_3ClO_2} + \underset{\text{Hydrochloric acid.}}{HCl.}$$

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Nitric acid.}}{HNO_3} = \underset{\text{Nitro-benzene.}}{C_6H_5NO_2} + \underset{\text{Water.}}{H_2O.}$$

Derivatives. This term is applied to bodies derived from others by some kind of decomposition, generally by substitution. Thus, nitro-benzene is a derivative of benzene; chloroform, $CHCl_3$, is a derivative of methane, CH_4, obtained from the latter by replacement of three atoms of hydrogen by the same number of atoms of chlorine.

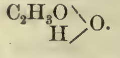
Isomerism. Two or more substances may have the same elements in the same proportion by weight (or the same centesimal composition), and yet be different bodies, showing different properties. Such substances are called isomeric bodies. Two kinds of isomerism are distinguished, viz., metamerism and polymerism.

Metamerism. Substances are metameric when their molecules contain equal numbers of atoms of the same elements. Thus, the oils of juniper, turpentine, lemon, etc., all have the molecular formula $C_{10}H_{16}$, and yet they have different physical properties, and may be distinguished by their odor, by their action on polarized light, etc.

The explanation given regarding this difference of properties is, that the atoms are arranged differently within the molecule. In some cases this arrangement is as yet unknown, in other cases structural or graphic formulas showing this atomic arrangement may be given.

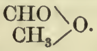
For instance: Acetic acid and methyl formate both have the composition $C_2H_4O_2$, but the arrangement of the atoms (or the structure) is very different, as shown by the formulas:

Acetic acid.



$$\left.\begin{array}{r}C_2H_3O\\H\end{array}\right\rangle O.$$

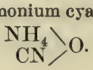
Methyl formate.



$$\left.\begin{array}{r}CHO\\CH_3\end{array}\right\rangle O.$$

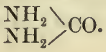
As another instance may be mentioned the compound CN_2H_4O, which represents either ammonium cyanate or urea:

Ammonium cyanate.



$$\left.\begin{array}{r}NH_4\\CN\end{array}\right\rangle O.$$

Urea.



$$\left.\begin{array}{r}NH_2\\NH_2\end{array}\right\rangle CO.$$

Polymerism. Substances are said to be polymeric when they have the same centesimal composition, but a different molecular weight, or, in other words, when one substance contains some multiple of the number of each of the atoms contained in the molecule of the other.

For instance, some volatile oils have the composition $C_{20}H_{32}$, which is double the number of atoms contained in oil of turpentine, $C_{10}H_{16}$; acetylene, C_2H_2, is polymeric with benzene, C_6H_6; acetic acid, $C_2H_4O_2$, is polymeric with grape-sugar, $C_6H_{12}O_6$, etc.

Various modes of decomposition. The principal changes which a molecule may suffer are as follows:

a. The atoms may arrange themselves differently within the molecule. Ammonium cyanate, NH_4CNO, is easily converted into urea, $CO(NH_2)_2$.

b. A molecule may split up into two or more molecules. For instance:

$$\underset{\text{Grape-sugar.}}{C_6H_{12}O_6} = \underset{\text{Alcohol.}}{2C_2H_6O} + \underset{\text{Carbon dioxide.}}{2CO_2}.$$

c. Two molecules, either of the same kind, or of different substances, may unite together directly:

$$\underset{\text{Ethylene.}}{C_2H_4} + \underset{\text{Bromine.}}{2Br} = \underset{\text{Ethylene bromide.}}{C_2H_4Br_2}.$$

d. Atoms may be removed from a compound without replacing them by other atoms:

$$\underset{\text{Alcohol.}}{C_2H_6O} + \underset{\text{Oxygen.}}{O} = \underset{\text{Aldehyde.}}{C_2H_4O} + \underset{\text{Water.}}{H_2O}.$$

e. Atoms may be removed and replaced by others at the same time (substitution):

$$\underset{\text{Acetic acid.}}{C_2H_4O_2} + \underset{\text{Chlorine.}}{2Cl} = \underset{\substack{\text{Monochloracetic}\\\text{acid.}}}{C_2H_3ClO_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{HCl}.$$

Action of heat upon organic substances. As a general rule, organic bodies are distinguished by the facility with which they decompose under the influence of heat or chemical agents; the more complex the body is, the more easily does it undergo decomposition or transformation.

Heat acts differently upon organic substances, some of which may be volatilized without decomposition, whilst others are decomposed by heat with generation of volatile products. This process of heating non-volatile organic substances in such a manner that the oxygen of the atmospheric air has no excess, and to such an extent that decomposition takes place, is called *dry or destructive distillation.*

The nature of the products formed during this process varies not only with the nature of the substance heated, but also with the temperature applied during the operation. The products formed by destructive distillation are invariably less complex in composition, that is, have a smaller number of atoms in the molecule, than the substance which suffered decomposition; in other words, a complex molecule is split up into two or more molecules less complex in composition.

Otherwise, the products formed show a great variety of properties; some are gases, others volatile liquids or solids, some are neutral, others basic or acid substances. In most cases of destructive distillation a non-volatile residue is left, which is nearly pure carbon.

Action of oxygen upon organic substances. Combustion. Decay. All organic substances are capable of oxidation, which takes place either rapidly with the evolution of heat and light and is called *combustion*, or it takes place slowly without the emission of light, and is called *slow combustion* or *decay*. The heat generated during the decay of a substance is the same as that generated by burning the substance; but as this heat is liberated in the first instance during weeks, months, or perhaps years, its generation is so slow that it can scarcely be noticed.

No organic substance found or formed in nature contains a sufficient quantity of oxygen to cause the complete combustion of the combustible elements (carbon and hydrogen) present; by artificial processes such substances may, however, be produced, and are then either highly combustible or even explosive.

During common combustion, provided an excess of atmospheric oxygen be present, the total quantity of carbon is converted into carbon dioxide, hydrogen into water, sulphur and phosphorus into sulphuric and phosphoric acids, while nitrogen is generally liberated in the elementary state.

During the process of decay the compounds mentioned above are produced finally, although many intermediate products are generated. For instance: If a piece of wood be burnt, complete oxidation takes place; intermediate products also are formed chiefly in consequence of the destructive distillation of a portion of the wood, but they are consumed almost as fast as they are produced, as was mentioned in connection with the consideration of flame. Again, when a piece of wood is exposed to the action of the atmosphere, it slowly burns or decays. The intermediate products formed in this case are entirely different from those produced during common combustion.

Common alcohol has the composition C_2H_6O; in burning, it requires six atoms of oxygen, when it is converted into carbon dioxide and water:

$$C_2H_6O + 6O = 2CO_2 + 3H_2O.$$

But alcohol may also undergo slow oxidation, in which case oxygen first removes hydrogen, with which it combines to form water, whilst at the same time a compound known as acetic aldehyde, C_2H_4O, is formed:

$$C_2H_6O + O = C_2H_4O + H_2O.$$

This aldehyde, when further acted upon by oxygen, takes up an atom of this element, thereby forming acetic acid:

$$C_2H_4O + O = C_2H_4O_2$$

The three instances given above illustrate the action of oxygen upon organic substances, which action may consist in a mere removal of hydrogen, in a replacement of hydrogen by oxygen, or in an oxidation of both the carbon and hydrogen, and also of sulphur and phosphorus, if they be present.

An organic substance, when perfectly dry and exposed to dry air only, may not suffer decay for a long time (not even for centuries), but in the presence of moisture and air this oxidizing action takes place almost invariably.

Besides the slow oxidation or decay which all dead organic matter undergoes in the presence of moisture, there is another kind of slow oxidation, called respiration, which takes place in the living animal; this process will be more fully considered in the physiological part of this book.

Fermentation and putrefaction. These terms are applied to peculiar kinds of decomposition, by which the molecules of certain organic substances are split up into two or more molecules of a less complicated composition. These decompositions take place when three factors are simultaneously acting upon the organic substance. These factors are: presence of moisture, favorable temperature, and presence of a substance generally termed ferment.

The most favorable temperature for these decompositions lies between 25° and 40° C. (77° and 104° F.), but they may take place at lower or higher temperatures. No substance, however, will either ferment or putrefy at or below the freezing-point, or at or above the boiling-point.

The nature of the various ferments differs widely, and their true action cannot, in many cases, be explained; what we do know is, that the presence of comparatively small (often minute) quantities of one substance (the ferment) is sufficient to cause the decomposition of large quantities of certain organic substances, the ferment itself suffering often no apparent change during this decomposition. Ferments may be divided into two classes: 1. Soluble ferments, which are in most cases nitrogenous substances, closely related to the proteids; 2. Living micro-organisms of either vegetable or animal origin.

The nature of the ferment generally determines the nature of the decomposition which a substance suffers, or, in other words, one and the same substance will under the influence of one ferment decompose with liberation of certain products, while a second ferment causes other products to be evolved. Sugar, for instance, under the influence of yeast, is converted into alcohol and carbon dioxide, while under the influence of certain other ferments it is converted into lactic acid.

The difference between fermentation and putrefaction is, that the first term is used in those cases where the decomposing substance contains carbon, hydrogen, and oxygen only, while substances containing, in addition to these three elements, either nitrogen or sulphur (or both) undergo putrefaction. The two last-named elements are generally evolved as ammonia or derivatives of ammonia and hydrogen sulphide, which gases give rise to an offensive odor.

Sugar, having the composition $C_6H_{12}O_6$, undergoes fermentation, whilst albuminous substances which contain also nitrogen and sulphur putrefy.

The oxygen of the air takes no part in either fermentation or putrefaction, but the presence or absence of atmospheric air may cause or prevent decomposition, inasmuch as the atmosphere is filled with millions of minute germs of organic nature, which germs may act as ferments when in contact with organic matter under favorable conditions.

Whenever organic bodies (a dead animal, for instance) undergo decomposition in nature, the processes of fermentation and putrefaction are generally accompanied by oxidation or decay.

The conditions under which a substance will ferment or putrefy have been stated above, and the non-fulfilment of these conditions enables us to prevent decomposition artificially.

Thus, we freeze substances (meat); or expel all water from or dry them (fruit, etc.), in order to prevent decomposition. The action of the ferments is counteracted either by the so-called antiseptic agents (salt, carbolic or salicylic acid, etc.) which are incompatible with organic life, or by excluding the air, and with it the ferments, by enclosing the substances in air-tight vessels (glass jars, tin cans, etc.), which, when filled, are heated sufficiently to destroy any germs which may have been present.

Antiseptics and disinfectants. While the term *antiseptics* is applied to those substances which retard or prevent fermentation and putrefaction, the term *disinfectants* refers to those agents actually destroying the organisms which are the causes of these decompositions. If we assume that all infectious diseases are due to micro-organisms, or germs of various kinds, disinfectants may be considered as equivalent to *germicides.* Disinfectants are generally antiseptics also, but the latter are not in all cases disinfectants. The solution of a substance of certain strength may act as a disinfectant and antiseptic, while the same solution diluted further may act as an antiseptic only, but not as a disinfectant.

Deodorizers are those substances which convert the strongly smelling products of decomposition into inodorous compounds. Strong oxidizing agents are generally good deodorizers, as, for instance, chlorine, potassium permanganate, hydrogen dioxide, etc. Among the best antiseptics and disinfectants are chlorine (generally used in the form of a 4 per cent. solution of hypochlorite of calcium), mercuric chloride (a solution of 1 : 500 or 1 : 1000), carbolic acid (a 5 per cent. solution), and some other substances.

Action of chlorine and bromine. These two elements act upon organic substances (similarly to oxygen) in three different ways, viz., they either (rarely, however) combine directly with the organic substance, or remove hydrogen, or replace hydrogen. The following equations illustrate this action :

$$\underset{\text{Ethylene.}}{C_2H_4} + \underset{\text{Bromine.}}{2Br} = \underset{\text{Ethylene bromide.}}{C_2H_4Br_2.}$$

$$\underset{\text{Ethyl alcohol.}}{C_2H_6O} + \underset{\text{Chlorine.}}{2Cl} = \underset{\text{Aldehyde.}}{C_2H_4O} + \underset{\text{Hydrochloric acid.}}{2HCl.}$$

$$\underset{\text{Acetic acid.}}{C_2H_4O_2} + \underset{\text{Chlorine.}}{2Cl} = \underset{\substack{\text{Monochloracetic}\\ \text{acid.}}}{C_2H_3ClO_2} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{HCl.}$$

In the presence of water, chlorine and bromine often act as oxidizing agents by combining with the hydrogen of the water and liberating oxygen ; iodine may act in a similar manner as an oxidizing agent, but it rarely acts directly by substitution.

Action of nitric acid. This substance acts either by direct combination with organic bases forming salts, or as an oxidizing agent, or by substitution of nitryl, NO_2, for hydrogen. As instances of the latter action may be mentioned the formation of nitro-benzene and nitro-cellulose :

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Nitric acid.}}{HNO_3} = \underset{\text{Nitro-benzene.}}{C_6H_5NO_2} + \underset{\text{Water.}}{H_2O}.$$

$$\underset{\text{Cellulose.}}{C_6H_{10}O_5} + \underset{\text{Nitric acid.}}{3HNO_3} = \underset{\text{Trinitro-cellulose.}}{C_6H_7(NO_2)_3O_5} + \underset{\text{Water.}}{3H_2O}.$$

The additional quantity of oxygen thus introduced into the molecules renders them highly combustible, or even explosive.

Action of dehydrating agents. Substances having a great affinity for water, such as strong sulphuric acid, phosphoric oxide, and others, act upon many organic substances by removing from them the elements of hydrogen and oxygen, and combining with the water formed, while, at the same time, frequently dark or even black compounds are formed, which consist largely of carbon. The black color imparted to sulphuric acid by organic matter depends on this action.

Action of alkalies. The hydroxides of potassium and sodium act in various ways on organic substances.

In some cases direct combiuation takes place :

$$\underset{\text{Carbonic oxide.}}{CO} + \underset{\substack{\text{Potassium}\\\text{hydroxide.}}}{KOH} = \underset{\substack{\text{Potassium}\\\text{formate.}}}{KCHO_2}.$$

Salts are formed :

$$\underset{\substack{\text{Acetic}\\\text{acid.}}}{C_2H_4O_2} + \underset{\substack{\text{Sodium}\\\text{hydroxide.}}}{NaOH} = \underset{\substack{\text{Sodium}\\\text{acetate.}}}{NaC_2H_3O_2} + \underset{\text{Water.}}{H_2O}.$$

Fats are decomposed with the formation of soap :

$$\underset{\text{Oleate of glyceril.}}{C_3H_5(C_{18}H_{33}O_2)_3} + \underset{\text{Sodium hydroxide.}}{3NaOH} = \underset{\text{Glycerin.}}{C_3H_5(HO)_3} + \underset{\text{Sodium oleate.}}{3NaC_{18}H_{33}O_2}.$$

Oxidation takes place, while hydrogen is liberated :

$$\underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{C_2H_6O} + \underset{\substack{\text{Potassium}\\\text{hydroxide.}}}{KOH} = \underset{\substack{\text{Potassium}\\\text{acetate.}}}{KC_2H_3O_2} + \underset{\text{Hydrogen.}}{4H}.$$

From compounds containing nitrogen, ammonia is evolved :

$$\underset{\text{Acetamide.}}{NH_2C_2H_3O} + \underset{\substack{\text{Potassium}\\\text{hydroxide.}}}{KOH} = \underset{\substack{\text{Potassium}\\\text{acetate.}}}{KC_2H_3O_2} + \underset{\text{Ammonia.}}{NH_3}.$$

Action of reducing agents. Deoxidizing or reducing agents, especially hydrogen in the nascent state, act upon organic substances either by direct combination :

$$\underset{\text{Ethene oxide.}}{C_2H_4O} + 2H = \underset{\text{Ethyl alcohol.}}{C_2H_6O}.$$

or by removing oxygen (and also chlorine or bromine):

$$\underset{\text{Benzoic acid.}}{C_7H_6O_2} + 2H = \underset{\text{Benzoic aldehyde.}}{C_7H_6O} + H_2O.$$

In some cases hydrogen replaces oxygen:

$$\underset{\text{Nitro-benzene.}}{C_6H_5NO_2} + 6H = \underset{\text{Aniline.}}{C_6H_5NH_2} + 2H_2O.$$

Classification of organic compounds. There are great difficulties in arranging the immense number of organic substances properly, and in such a manner that natural groups are formed the members of which are similar in composition and possess like properties.

Various modes of classification have been proposed, some of which, however, are so complicated that the beginner will find it difficult to make use of them. The grouping of organic substances here adopted, while far from being perfect, has the advantages of being simple, easily understood, and remembered.

1. *Hydrocarbons.* All compounds containing the two elements carbon and hydrogen only. For instance, CH_4, C_6H_6, $C_{10}H_{16}$, etc.

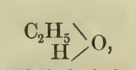
2. *Alcohols.* These are unsaturated hydrocarbons or hydrocarbon residues in combination with hydroxyl, OH. For instance, ethyl alcohol, $C_2H^{i}_5OH$, glycerin, $C_3H^{iii}_5(OH)_3$, etc.

3. *Aldehydes.* Unsaturated hydrocarbons in combination with the radical COH; they are compounds intermediate between alcohols and acids, or alcohols from which hydrogen has been removed. For instance:

$$\underset{\text{Ethyl alcohol.}}{C_2H_6O,} \qquad \underset{\text{Aldehyde.}}{C_2H_4O,} \qquad \underset{\text{Acetic acid.}}{C_2H_4O_2.}$$

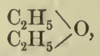
4. *Organic acids.* Unsaturated hydrocarbons in combination with carboxyl, a radical having the composition CO_2H, or compounds formed by replacement of hydrogen in hydrocarbons by carboxyl. Instances: Acetic acid, CH_3CO_2H; pyrotartaric acid, $C_3H_6(CO_2H)_2$.

5. *Ethers.* Compounds formed from alcohols by replacement of the hydrogen of the hydroxyl by other unsaturated hydrocarbons, or, what is the same, by other alcohol radicals. For instance:



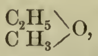
$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\rangle O,$$

Ethyl alcohol.



$$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle O,$$

Ethyl ether.

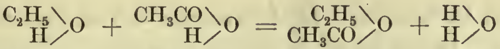


$$\left.\begin{matrix}C_2H_5\\CH_3\end{matrix}\right\rangle O,$$

Ethyl-methyl ether.

6. *Compound ethers or esters.* Formed from alcohols by replacement of the hydrogen of the hydroxyl by acid radicals, or from acids

by replacement of the hydrogen of carboxyl by alcohol radicals. For instance:



$$\underset{\text{Ethyl alcohol.}}{\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\rangle O} + \underset{\text{Acetic acid.}}{\left.\begin{matrix}CH_3CO\\H\end{matrix}\right\rangle O} = \underset{\text{Acetic ether.}}{\left.\begin{matrix}C_2H_5\\CH_3CO\end{matrix}\right\rangle O} + \underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\rangle O}$$

The various fats belong to this group of compound ethers.

7. *Carbohydrates.* (Sugars, starch, cellulose, etc.) These compounds contain 6 atoms of carbon (or a multiple of 6) in the molecule, and hydrogen and oxygen in the proportion of 2 atoms of hydrogen to 1 atom of oxygen, or in the proportion to form water. Most carbohydrates are capable of fermentation, or of being easily converted into fermentable bodies. Instances: $C_6H_{12}O_6$, $C_6H_{10}O_5$, etc.

Glucosides are substances the molecules of which may be split up in such a manner that several new bodies are formed, one of which is sugar.

8. *Amines and amides.* Substances formed by replacement of hydrogen in ammonia by alcohol or acid radicals. For instance: ethyl amine, $NH_2.C_2H_5$, urea, $N_2H_4.CO$, etc. The alkaloids belong to this group.

9. *Cyanogen and its compounds.* Substances containing the radical cyanogen, CN. For instance: potassium cyanide, KCN.

10. *Proteids or albuminous substances.* These, besides carbon, hydrogen, and oxygen, always contain nitrogen and sulphur, sometimes also other elements. Instances: albumin, casein, fibrin, etc.

In connection with each of these groups have to be considered the derivatives obtained from them directly or indirectly.

As all those organic compounds the constitution of which has been explained may be looked upon as derivatives of either methane, CH_4, or benzene, C_6H_6, a separation of organic compounds is made into two large classes, each one embodying all the derivatives of one of the two hydrocarbons named. The derivatives of methane are termed *fatty compounds,* those of benzene *aromatic compounds.* Fatty compounds have representatives in each one of the above ten groups: aromatic compounds are missing in a few. As far as practicable, the two classes will be considered separately, because the properties of fatty and aromatic compounds differ so widely, in some respects, that this method of studying the nature of carbon compounds is to be preferred.

QUESTIONS.—381. Explain the term residue or radical. 382. What is understood by the expression chain, when used in chemistry? 383. What are the characteristics of an homologous series? 384. Give an explanation of the

40. HYDROCARBONS.

Occurrence in nature. Hydrocarbons are seldom derived from animal sources, being more frequently products of vegetable life; thus, the various essential oils (oil of turpentine and others) of the composition $C_{10}H_{16}$ or $C_{20}H_{32}$ are frequently found in plants, where they are formed from carbon dioxide and water:

$$10CO_2 + 8H_2O = C_{10}H_{16} + 28O.$$

This equation, whilst showing the possibility of the formation of an essential oil in the plant, must not be taken to mean that 10 molecules of carbon dioxide and 8 molecules of water are simultaneously decomposed, with the production of a hydrocarbon; on the contrary, we know that many intermediate substances are formed, and the formula simply gives the final result, not the intermediate stages of the process.

Other hydrocarbons are found in nature as products of the decomposition of organic matter. Thus methane, CH_4, is generally formed during the decay of organic matter in the presence of moisture; the higher members of the methane series are found in crude coal-oil.

Formation of hydrocarbons. It is difficult to combine the two elements carbon and hydrogen directly; as an instance of such direct combination may be mentioned acetylene, C_2H_2, which is formed when electric sparks pass between electrodes of carbon in an atmosphere of hydrogen.

Many hydrocarbons are obtained by destructive distillation of organic matter, and their nature depends on the composition of the material used and upon the degree of heat applied for the decomposition. Hydrocarbons may also be obtained by the decomposition (other than destructive distillation) of numerous organic bodies, such as alcohols, acids, amines, etc., and from derivatives of these substances.

The hydrocarbons found in nature are generally separated from other matter, as well as from each other, by the process known as

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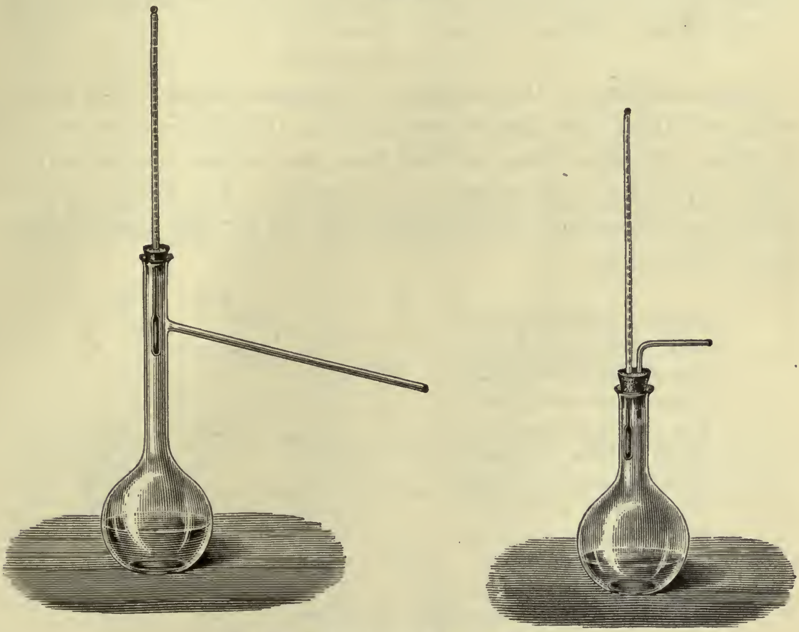
terms isomerism, metamerism, and polymerism. 385. How does heat act upon organic compounds? 386. What is destructive distillation? 387. State the difference between combustion, decay, fermentation, and putrefaction; what is the nature of these processes, and under what conditions do they take place? 388. How do chlorine, nitric acid, and alkalies act upon organic substances? 389. What is the action of hydrogen, and of dehydrating agents, upon organic substances? 390. Mention the chief groups of organic compounds.

fractional distillation. As the boiling-points of the various compounds differ more or less, they may be separated by carefully distilling off the compounds of lower boiling-points, while noting the temperature of the vapors above the boiling liquid by means of an inserted thermometer, and changing the receiver every time an increase of the boiling-point is noticed. This separation of volatile liquid, known as fractional distillation, is, however, not absolutely complete, because traces of substances having a higher boiling-point are simultaneously volatilized with the distilling substance.

FIG. 39.



Flasks arranged for fractional distillation.

For fractional distillation of small quantities of liquids as well as for the determination of boiling-points, flasks arranged like those shown in Fig. 39 may be used.

Properties of hydrocarbons. There are no other two elements which combine together in so many proportions as carbon and hydrogen. Several hundred hydrocarbons are known, many of which form either homologous series or are metameric or polymeric.

Hydrocarbons occur either as gases, liquids, or solids. If the molecule contains not over 4 atoms of carbon, the compound is generally a gas at the ordinary temperature; if it contains from 4 to 10 or 12 atoms of carbon, it is a liquid; and if it contains a yet higher number of carbon atoms, it is generally a solid.

All hydrocarbons may be volatilized without decomposition, all are colorless substances, and many have a peculiar and often characteristic odor; they are generally insoluble in water but soluble in alcohol, ether, disulphide of carbon, etc.

In regard to chemical properties, it may be said that hydrocarbons are neutral substances, behaving rather indifferently toward most other chemical agents. Most of them are, however, oxidized by the oxygen of the air, by which process liquid hydrocarbons are often converted into solids.

Hydrocarbons of the paraffin or methane series. The hydrocarbons having the general composition C_nH_{2n+2} are known as paraffins, the name being derived from the higher members of the series which form the paraffin of commerce. The following table gives the composition, boiling-points, etc., of the first sixteen members of this series:

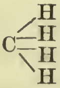
		B. P.	Sp. gr.
Methyl hydride or methane,	CH_4	gases.	
Ethyl hydride or ethane,	C_2H_6		
Propyl hydride or propane,	C_3H_8		
Butyl hydride or butane,	C_4H_{10}	1° C.	
Amyl hydride or pentane,	C_5H_{12}	38	0.628
Hexyl hydride or hexane,	C_6H_{14}	70	0.669
Heptyl hydride or heptane,	C_7H_{16}	99	0.690
Octyl hydride or octane,	C_8H_{18}	125	0.726
Nonyl hydride or nonane,	C_9H_{20}	148	0.741
Decyl hydride or decane,	$C_{10}H_{22}$	166	0.757
Undecyl hydride or undecane,	$C_{11}H_{24}$	184	0.766
Dodecyl hydride or dodecane,	$C_{12}H_{26}$	202	0.778
Tridecyl hydride or tridecane,	$C_{13}H_{28}$	218	0.796
Tetradecyl hydride or tetradecane,	$C_{14}H_{30}$	236	0.809
Pentadecyl hydride or pentadecane,	$C_{15}H_{32}$	258	0.825
Hexadecyl hydride or hexadecane,	$C_{16}H_{34}$	280	
etc.			

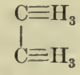
The above table shows that the paraffins form an homologous series; the first four members are gases, most of the others liquids, regularly increasing in specific gravity, boiling-point, viscidity, and vapor density, as their molecular weight becomes greater.

The paraffins are saturated hydrocarbons, the constitution of which has been already explained; they are incapable of uniting directly with monatomic elements or residues, but they easily yield substitution-derivatives when subjected to the action of chlorine or bromine.

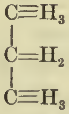
Most of the paraffins are known in two (or even more) modifications; there are, therefore, other homologous series of hydrocarbons of the same composition as the above normal paraffins, which show some difference from the normal paraffins in boiling-points and other properties. In these isomeric paraffins the atoms are arranged differently from those in the normal hydrocarbons, which fact may be proven by the difference in decomposition which these substances suffer when acted upon by chemical agents.

No isomeric hydrocarbons of the first three members of the paraffin series are known, which fact is in accordance with our present theories. Assuming that the quadrivalent carbon atoms exert their full valence, and that they are held together by one atomicity only, we can arrange the atoms in the compounds, CH_4, C_2H_6, and C_3H_8, not otherwise than thus:



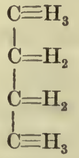


$$\begin{array}{c} C\equiv H_3 \\ | \\ C\equiv H_3 \end{array}$$

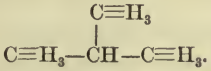


$$\begin{array}{c} C\equiv H_3 \\ | \\ C=H_2 \\ | \\ C\equiv H_3 \end{array}$$

In the next compound, butane, C_4H_{10}, we have two possibilities explaining the structure of the molecule, namely, these:



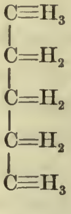
$$\begin{array}{c} C\equiv H_3 \\ | \\ C=H_2 \\ | \\ C=H_2 \\ | \\ C\equiv H_3 \end{array}$$



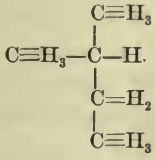
$$\begin{array}{rcl} & C\equiv H_3 & \\ & | & \\ C\equiv H_3- & CH & -C\equiv H_3. \end{array}$$

Both these compounds are known, and termed normal butane and isobutane, respectively.

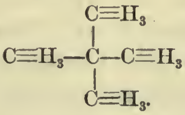
The next member, pentane, C_5H_{12}, shows three possibilities of constitution, thus:



$$\begin{array}{c} C\equiv H_3 \\ | \\ C=H_2 \\ | \\ C=H_2 \\ | \\ C=H_2 \\ | \\ C\equiv H_3 \end{array}$$



$$\begin{array}{rl} & C\equiv H_3 \\ & | \\ C\equiv H_3- & C-H. \\ & | \\ & C=H_2 \\ & | \\ & C\equiv H_3 \end{array}$$



$$\begin{array}{rcl} & C\equiv H_3 & \\ & | & \\ C\equiv H_3- & C & -C\equiv H_3 \\ & | & \\ & C\equiv H_3. & \end{array}$$

These compounds also are known. With the higher members of the paraffins the number of possible isomeres rises rapidly according to the law of permutation, so that we have of the seventh member 9, of the tenth 75, and of the thirteenth member 799, possible isomeric hydrocarbons.

Methane, CH_4 (*Marsh-gas, Fire-damp*). This hydrocarbon has been spoken of in Chapter 13, where it was stated that it is a colorless, combustible gas, which is formed by the decay of organic matter in the presence of moisture, during the formation of coal in the interior of the earth, and by the destructive distillation of various organic matters. Methane is of special interest, because it is the compound from which thousands of other substances are derived. It may be made by the action of inorganic substances upon one another; for instance, by passing a mixture of steam and carbon disulphide over copper heated to red heat, when the following change takes place:

$$6Cu + CS_2 + 2H_2O = 2Cu_2S + 2CuO + CH_4$$

Bearing in mind that carbon disulphide, as well as water, may be obtained by direct union of the elements, it is evident that methane may be formed indirectly, by means of the above method, from the elements carbon and hydrogen.

Experiment 40. Use apparatus shown in Fig. 5, page 37, omitting the bent tube B. Mix in a mortar 20 grammes of sodium acetate with 20 grammes of potassium (or sodium) hydroxide and 30 grammes of calcium hydroxide; fill with this mixture the tube A, which should be made of glass fusing with difficulty, or of so-called "combustion tubing;" apply heat and collect the gas over water. The decomposition takes place thus:

$$NaC_2H_3O_2 + NaOH = Na_2CO_3 + CH_4.$$

Ignite the gas, and notice that its flame is but slightly luminous. Mix some of the gas in a wide-mouth cylinder, of not more than about 200 c.c. capacity, with an equal volume of air and ignite. Repeat this experiment with mixtures of one volume of methane with 2, 4, 6, 8, and 10 volumes of atmospheric air. Which mixture is most explosive, and why? How many volumes of oxygen and how many volumes of atmospheric air are needed for the complete combustion of one volume of methane?

Coal. As methane is one of the products generated during the formation of coal, it may be well to consider this process here briefly.

The various substances classed togther under the name of *coal* consist principally of carbon, associated with smaller quantities of hydrogen, oxygen, nitrogen, sulphur, and certain inorganic mineral matters which compose the ash. Coal is formed from buried vegetable matter by a process of decomposition which is partly a fermentation, partly a decay, and chiefly a slow destructive distillation, the heat for this latter process being derived from the interior of the earth, or by the decomposition itself.

The principal constituent of the organic matter furnishing coal is wood (or woody fibre, cellulose), and a comparison of the composition of this substance with the various kinds of coal gradually formed will help to illustrate the chemical change taking place:

	Carbon.	Hydrogen.	Oxygen.
Wood	100	12.18	83.07
Peat	100	9.85	55.67
Lignite	100	8.37	42.42
Bituminous coal	100	6.12	21.23
Anthracite coal	100	2.84	1.74

This table shows a progressive diminution in the proportions of hydrogen and oxygen during the passage from wood to anthracite. These two elements must, therefore, be eliminated in some form of combination which allows them to move, viz., as gases or liquids. The gases formed are chiefly carbon dioxide (which finds its way through the rocks and soils to the surface either in the gaseous state or after having been absorbed by water in the form of carbonic acid springs) and methane, known to coal-miners as fire-damp, frequently causing the formation of explosive gas mixtures in the coal mines, or escaping, like carbon dioxide, through fissures to the surface of the earth, where it may be ignited.

Natural gas. While methane and other combustible gases are undoubtedly formed during the formation of coal, the gas mixture now generally termed natural gas (a mixture of methane, ethane, propane, hydrogen, and a few other gases), and used largely for heating and illuminating purposes, is most likely a product of the complete decomposition of vegetable and animal matter which has been precipitated from water, simultaneously with inorganic matter, during the formation of certain rocks, chiefly slate and limestone. The decomposition of this organic matter has been so complete that the gaseous decomposition-products only are left, but no, or very little of, solid residue similar to coal.

Coal-oil, Petroleum. Similar to natural gas, coal-oil is a product of the decomposition of organic matter, most likely of the fats and oils of fish and other aquatic animals. While the albuminous constituents of dead animal matter decompose rapidly, fats are comparatively stable. These oils and fats, after being precipitated simultaneously with other organic and inorganic matter from water, have formed by their decomposition (which was chiefly a destructive distillation) the liquid we call coal-oil or petroleum.

Coal-oil is a mixture of the various liquid paraffins, containing often in solution the gaseous and solid members of this group, as also small quantities of coloring and other matter. The boiling-points of the constituents of coal-oil lie between 0° and 300° C. (32° and

572° F.), or even higher. The crude oil is purified, by treating it with sulphuric acid, followed by other processes of refining, and finally by fractional distillation, in order to separate the members of low boiling-points from those of higher boiling-points.

The hydrocarbons of low boiling-points, chiefly a mixture of C_5H_{12} and C_6H_{14}, are official, under the name of *benzin* or *petroleum-ether*, which name must not be confounded with benzene or benzol, C_6H_6. According to the U. S. P., benzin should have a specific gravity from 0.67 to 0.675, and a boiling-point of 50° to 60° C. (122° to 140°F.).

Other similar liquids are sold in the market under the name of *rhigoline*, B. P. about 21° C. (70° F.) and *gasoline*, B. P. about 75° C. (167° F.); they are highly inflammable.

The paraffins distilling between 150° and 250° C. (302° and 408° F.) constitute the common *illuminating oil*, various kinds of which are sold as kerosene, paraffin oil, astral oil, mineral sperm oil, etc. The danger which arises in the use of coal-oil as an illuminating agent is caused by the use of oils which have not been sufficiently freed from the more volatile members of the series, which, when but slightly heated (or even at ordinary temperature) will vaporize, and upon mixing with atmospheric air, form explosive mixtures. An oil to be safely used for illuminating purposes in common lamps should not give off inflammable vapors (or flash) below 49° C. (120° F.).

Experiment 41. Various forms of apparatus are used for the exact determination of the flashing-point; students may determine it approximately by operating as follows: Fill a cylinder (about one inch in diameter and six inches high) two-thirds with coal-oil, suspend in the oil a thermometer, place the cylinder in a vessel with water (water-bath), keeping the level of the oil even with that of the water, and heat the latter slowly. Cover the cylinder loosely with a piece of pasteboard, and when the thermometer indicates a rise in temperature pass a small flame quickly over the mouth of the cylinder after having removed the pasteboard. Repeat this operation, from degree to degree, until a bluish flame is noticed running down to the surface of the oil. The temperature at which this takes place indicates the flashing-point.

After the illuminating oil has been distilled off, a mixture of substances passes over, which is used for lubricating purposes or furnishes, after having been purified by treatment with bone-black, the official articles known as *soft* and *hard petrolatum*. Both are fat-like masses, more or less fluorescent, varying in color from white to yellowish or yellow, and almost without odor or taste. The article sold as *vaseline* is practically identical with soft petrolatum.

Liquid petrolatum of the U. S. P. is a petroleum of a specific gravity 0.875 to 0.945.

A mixture of the highest and solid members of the paraffin series distilling at a temperature about 350° C. (662° F.) is known as *paraffin*, a white, crystalline substance used for candles, etc.; it fuses at about 75° C. (167° F.).

Illuminating gas is a mixture of gases obtained by the destructive distillation of coal (or wood) in iron retorts, with subsequent purification of the gases generated. The constituents of coal have been mentioned above. The products formed from it during its destructive distillation are very numerous; the following are the most important:

Gases	Hydrogen	H.
	Methane	CH_4.
	Ethene	C_2H_4.
	Acetylene	C_2H_2.
	Nitrogen	N.
	Ammonia	NH_3.
	Carbonic oxide	CO.
	Carbon dioxide	CO_2.
	Hydrosulphuric acid	H_2S.
	Hydrocyanic acid	HCN.

				B. P.
Coal-tar	Liquids	Benzene	C_6H_6	80°
		Toluene	C_7H_8	110
		Aniline	$C_6H_5NH_2$	132
		Acetic acid	$C_2H_4O_2$	117
		Water	H_2O	100
	Solids	Carbolic acid	C_6H_6O	188
		Kresylic acid	C_7H_8O	201
		Naphtalene	$C_{10}H_8$	220
		Anthracene	$C_{14}H_{10}$	360
		Paraffin	$C_{16}H_{34}$	280

Solid residue: Coke, chiefly carbon and inorganic matter.

The gases are purified by condensing ammonia (and some other gases) in water, carbon dioxide and hydrosulphuric acid in calcium hydroxide. The following is the composition of a purified illuminating gas obtained from cannel-coal:

Hydrogen	46 volumes.
Methane	41 "
Ethene	6 "
Carbonic oxide	4 "
Carbon dioxide	2 "
Nitrogen	1 volume.

Experiment 42. Use apparatus shown in Fig. 5, page 37. Fill the combustion-tube A with sawdust (almost any other non-volatile organic matter may be used), apply heat and continue it as long as gases are evolved. Notice that by this process of *destructive distillation* are formed a gas (or gas mixture), which may be ignited, a dark, almost black liquid (tar), which condenses in the tube B, and that a residue is left which is chiefly carbon. The tarry liquid shows an acid reaction, due to acetic and other acids present.

Coal-tar, obtained as a by-product in the manufacture of illuminating gas, contains, as shown by the above table, many valuable substances, such as benzene, aniline, carbolic acid, paraffin, etc., which are separated from each other by making use of the difference in their boiling-points and specific gravities, or of their solubility or insolubility in various liquids, or, finally, of their basic, acid, or neutral properties.

Olefines. The hydrocarbons of the general formula C_nH_{2n} are termed olefines. To this series belong:

Ethene or ethylene	C_2H_4.
Propene or propylene	C_3H_6.
Butene or butylene	C_4H_8.
Pentene or amylene	C_5H_{10}.
Hexene or hexylene	C_6H_{12}.

Methene, CH_2, the lowest term of this series, is not known. The hydrocarbons of this series are not only homologous, but also polymeric with one another.

Of special interest is the first known member of the series, *ethene* or *olefiant gas*, on account of its normal occurrence in illuminating gas, as well as in most common flames, the luminosity of which depends greatly on the quantity of this compound present in the burning gas.

Benzene series, or aromatic hydrocarbons. The members of a series of hydrocarbons having the general composition C_nH_{2n-6}, and all the derivatives of this group, including the alcohols, acids, etc., are the substances spoken of before as aromatic compounds, and will be considered later.

Volatile or essential oils. The term essential oil is more a pharmaceutical than chemical term, and is used for a large number of liquids obtained from plants, and having in common the properties of being volatile, soluble in ether and alcohol, almost insoluble in water, and having a distinct and in most cases even highly characteristic odor. They stain paper as do fats or fat oils, from which they differ, however, by the disappearance after some time of the stain produced, while fats leave a permanent stain.

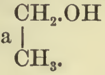
In their chemical composition essential oils differ widely; some are compound ethers, others aldehydes, but most of them are hydrocarbons or oxidized hydrocarbons, belonging to the benzene-derivatives, where they will be considered.

41. ALCOHOLS.

Constitution of alcohols. The old term "alcohol" originally indicated but one substance (ethyl alcohol), but is now applied to a large group of substances which may be looked upon as being derived from hydrocarbons by replacement of one, two, or more hydrogen atoms by hydroxyl, OH.

Any hydrocarbon may be converted into an alcohol radical by removal of one or more hydrogen atoms; methane, CH_4, for instance, is converted into methyl, CH_3, which, upon combining with hydroxyl, forms methyl alcohol, CH_3OH.

It has been shown before that the higher members of the paraffin series are capable of forming a number of isomeric compounds. Running parallel to the various series of hydrocarbons (and their isomeres) we have homologous series of alcohols. The isomeric alcohols also show properties different from one another, and yield different decomposition products. The isomeric alcohols are distinguished as *normal* or *primary*, *secondary* and *tertiary* alcohols; a normal alcohol is derived from a normal paraffin, and contains hydroxyl in the place of a hydrogen atom in a methyl group, the constitution of normal ethyl alcohol being, for instance, represented by the formula



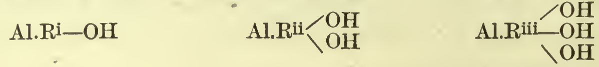
$$\begin{array}{l} CH_2.OH \\ | \\ CH_3. \end{array}$$

If hydroxyl replaces but one atom of hydrogen in a hydrocarbon, the alcohol is termed monatomic; diatomic and triatomic alcohols are formed by replacement of two or three hydrogen atoms respectively. (Diatomic alcohols are also termed *glycols*.) As an instance of a diatomic alcohol may be mentioned ethylene alcohol, $C_2H_4(OH)_2$, while glycerin, $C_3H_5(OH)_3$, is a triatomic alcohol.

QUESTIONS.—391. How do hydrocarbons occur in nature, and by what processes are they formed in nature or artificially? 392. State the general physical and chemical properties of hydrocarbons. 393. What is the general composition of the paraffins? 394. State the composition and properties of methane, and also the conditions under which it is formed in nature. 395. What is coal, what are its constituents, from what is it derived, and by what process has it been formed? 396. What is crude coal-oil, what is petroleum ether, and what is petrolatum? 397. How is illuminating gas manufactured, and what are its chief constituents? 398. Mention some of the important substances found in coal-tar. 399. Explain a method by which the flashing-point of coal-oil can be determined. 400. Which substances are termed volatile oils, and what are their properties?

Alcohols correspond in their composition to the hydroxides of inorganic substances; both classes of compounds containing hydroxyl, OH, which, in the case of alcohols, is in combination with residues containing carbon and hydrogen, in the case of inorganic hydroxides with metals, as, for instance, in potassium hydroxide, KOH.

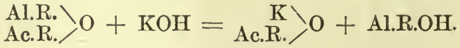
If we represent any unsaturated hydrocarbon by Al.R. (alcohol radical), the general formula of the alcohols will be:



	Monatomic alcohol.	Diatomic alcohol.	Triatomic alcohol.
	$\mathrm{Al.R^{i}{-}OH}$	$\mathrm{Al.R^{ii}}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}\right.$	$\mathrm{Al.R^{iii}}\begin{matrix}/\mathrm{OH}\\ -\mathrm{OH}\\ \backslash\mathrm{OH}\end{matrix}$
or	$\mathrm{Al.R^{i}OH}$	$\mathrm{Al.R^{ii}(OH)_2}$	$\mathrm{Al.R^{iii}(OH)_3}$
corresponding to	KOH	$\mathrm{Ca^{ii}(OH)_2}$	$\mathrm{Bi^{iii}(OH)_3}$.

Occurrence in nature. Alcohols are not found in nature in a free or uncombined state, but generally in combination with acids as compound ethers. Some plants, for instance, contain compound ethers mixed with volatile oils. The triatomic alcohol glycerin is a normal constituent of all fats or fatty oils, and is therefore found in many plants and in most animals.

Formation of alcohols. Alcohols are often produced by fermentation (ethyl alcohol from sugar), sometimes by destructive distillation (methyl alcohol from wood): they are obtained from compound ethers (which are compounds of acids and alcohols) by treating them with the alkali hydroxides, when the acid enters into combination with the alkali, whilst the alcohols are liberated according to the general formula:



$$\left.\begin{matrix}\mathrm{Al.R.}\\ \mathrm{Ac.R.}\end{matrix}\right\rangle\mathrm{O} + \mathrm{KOH} = \left.\begin{matrix}\mathrm{K}\\ \mathrm{Ac.R.}\end{matrix}\right\rangle\mathrm{O} + \mathrm{Al.R.OH.}$$

Alcohols may be obtained artificially by various processes, as, for instance, by treating hydrocarbons with chlorine, when the chloride of a hydrocarbon residue is formed, which may be decomposed by alkali hydroxides in order to replace the chlorine by hydroxyl, when an alcohol is formed. For instance:

$$\underset{\text{Ethane.}}{\mathrm{C_2H_6}} + 2\mathrm{Cl} = \underset{\text{Ethyl chloride.}}{\mathrm{C_2H_5Cl}} + \mathrm{HCl.}$$

$$\underset{\substack{\text{Ethyl}\\ \text{chloride.}}}{\mathrm{C_2H_5Cl}} + \underset{\substack{\text{Potassium}\\ \text{hydroxide.}}}{\mathrm{KOH}} = \underset{\substack{\text{Potassium}\\ \text{chloride.}}}{\mathrm{KCl}} + \underset{\substack{\text{Ethyl}\\ \text{alcohol.}}}{\mathrm{C_2H_5OH.}}$$

Properties of alcohols. Alcohols are generally colorless, neutral liquids; some of the higher members are solids, none is gaseous at the ordinary temperature. Most alcohols are specifically lighter than water; the lower members are soluble in or mix with water in all proportions; the higher members are less soluble, and, finally, insoluble. Most alcohols are volatile without decomposition; some of the highest members, however, decompose before being volatilized.

Although alcohols are neutral substances, it is possible to replace the hydrogen of the hydroxyl by metals, as, for instance, CH_3OH = methyl alcohol; CH_3ONa = sodium methyl oxide or sodium methylate.

The oxygen of alcohols may be replaced by sulphur, when compounds are formed known as *hydrosulphides* or *mercaptans;* these bodies may be obtained by treating the chlorides of hydrocarbon residues with potassium sulphydrate:

$$C_2H_5Cl + KSH = KCl + C_2H_5SH.$$

By replacement of the hydrogen of the hydroxyl in alcohols by alcohol radicals ethers are formed; by replacing the same hydrogen with acid radicals compound ethers are produced.

Monatomic normal alcohols of the general composition $C_nH_{2n+1}OH$ or $C_nH_{2n+2}O$.

		B. P.	
Methyl alcohol	$C\ H_3OH$	67° C.	
Ethyl "	C_2H_5OH	78	
Propyl "	C_3H_7OH	97	
Butyl "	C_4H_9OH	115	
Amyl "	$C_5H_{11}OH$	132	
Hexyl "	$C_6H_{13}OH$	150	
Heptyl "	$C_7H_{15}OH$	168	
Octyl "	$C_8H_{17}OH$	186	
Nonyl "	$C_9H_{19}OH$	204	
Cetyl "	$C_{16}H_{33}OH$	50	Fusing-point.
Ceryl "	$C_{27}H_{55}OH$	79	
Melissyl "	$C_{30}H_{61}OH$	85	

Methyl alcohol, CH_3OH (*Methyl hydroxide, Methyl alcohol, Wood-spirit, Wood-naphta*). Methyl alcohol is one of the many products obtained by the destructive distillation of wood. When pure it is a thin, colorless liquid, similar in smell and taste to ethyl alcohol; crude wood-spirit, which contains many impurities, has an offensive odor and a nauseous, burning taste. Methyl alcohol mixes in all proportions with water; it dissolves resins and volatile oils as freely as ethyl alcohol, and is often substituted for the latter for various purposes in the arts and manufactures.

Ethyl alcohol, $C_2H_5OH = 46$ (*Common alcohol, Ethyl hydroxide, Spirit*), may be obtained from ethene, C_2H_4, by addition of the elements of water, which may be accomplished by agitating ethene with strong sulphuric acid, when direct combination takes place and ethyl sulphuric acid is formed:

$$\underset{\text{Ethene.}}{C_2H_4} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Ethyl sulphuric acid.}}{C_2H_5HSO_4}.$$

Ethyl sulphuric acid mixed with water and distilled yields sulphuric acid and ethyl alcohol:

$$C_2H_5HSO_4 + H_2O = H_2SO_4 + C_2H_5OH.$$

Ethyl alcohol may also be obtained, as already mentioned, by treating ethyl chloride with potassium hydroxide:

$$C_2H_5Cl + KOH = KCl + C_2H_5OH.$$

While the above methods for obtaining alcohol are of scientific interest, there is but one mode of manufacturing it on a large scale, namely, by the fermentation of certain kinds of sugar, especially grape-sugar or glucose, $C_6H_{12}O_6$. A diluted solution of grape-sugar under the influence of certain ferments (yeast) suffers decomposition, yielding carbon dioxide and alcohol:

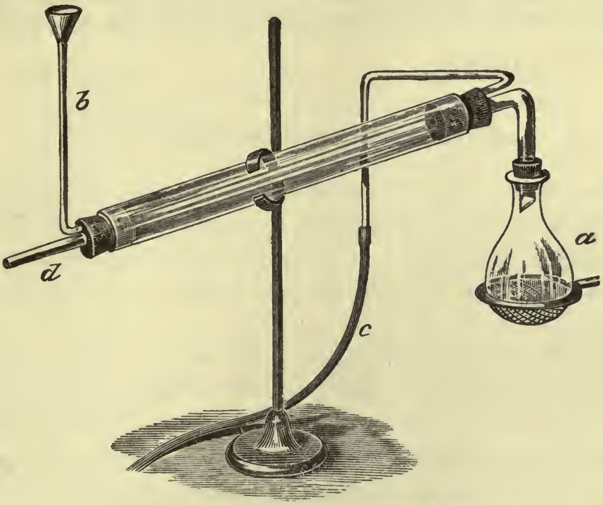
$$\underset{\text{Glucose.}}{C_6H_{12}O_6} = \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{2CO_2} + \underset{\substack{\text{Ethyl}\\ \text{alcohol.}}}{2C_2H_5OH}.$$

Experiment 43. To a solution of 25 grammes of commercial glucose (grape-sugar) in 1000 c.c. of water, add a little brewer's yeast and introduce this mixture into a flask. Attach to the flask, by means of a perforated cork, a bent glass tube leading into clear lime-water, contained in a small flask. After standing (a warm place should be selected in winter for this operation) a few hours fermentation will commence, which can be noticed by the evolution of carbon dioxide, which, in passing through the lime-water, causes the precipitation of calcium carbonate.

After fermentation ceases connect the flask with a condenser and distil over 50 to 100 c.c. of the liquid. Verify in the distilled portion the presence of alcohol by applying the tests mentioned below. For condensation of the distilling vapors a Liebig's condenser, represented in Fig. 40, may be used. This apparatus consists of a wide glass tube through which passes the narrow condensing tube, connected with the boiling-flask *a*. A constant current of cold water is obtained by allowing water to flow into *b*, and to escape by *c*. A small flask is placed under *d* for collecting the distillate.

By distilling the fermented liquid an alcohol is obtained containing large quantities of water; on distilling this dilute alcohol a second and a third time, collecting the first portions of the distilled liquid separately, an alcohol is obtained containing but little water. These last quantities of water, amounting to about 14 per cent., cannot be removed by simple distillation, but may be separated by mixing the alcohol with half its weight of calcium oxide, which combines with the water to form calcium hydroxide, from which the alcohol may now be separated by distillation.

FIG. 40.



Liebig's condenser with distilling-flask.

The alcohol thus obtained, and containing not more than 1 per cent. of water, is known as *pure, absolute,* or *real alcohol.* The *alcohol of the U. S. P.* contains 91 per cent. by weight, or 94 per cent. by volume of real alcohol, and has a specific gravity of 0.820 at 15° C. (59° F.). *The diluted alcohol* is made by mixing equal volumes of water and alcohol, and has a specific gravity of 0.936; it is identical with the *proof-spirit* of the U. S. Custom-house and Internal Revenue service.

Pure alcohol is a transparent, colorless, mobile, and volatile liquid, of a characteristic rather agreeable odor, and a burning taste; it boils at 78° C. (172° F.), has a specific gravity of 0.797, is of a neutral reaction, becomes syrupy at —110° C. (—166° F.), and solidifies at —130° C. (—202° F.); it burns with a non-luminous flame; when mixed with water a contraction of volume occurs, and heat is liberated; the attraction of alcohol for water is so great that strong alcohol absorbs moisture from the air or abstracts it from membranes, tissues, and other similar substances immersed in it; to this property are due its coagulating action on albumin and its preservative action on animal substances. The solvent powers of alcohol are very extensive, both for inorganic and organic substances; of the latter it readily dissolves essential oils, resins, alkaloids, and many other bodies, for which reason it is used in the manufacture of the numerous official tinctures, extracts, and fluid extracts.

Alcohol taken internally in a dilute form has intoxicating properties; pure alcohol acts poisonously; it lowers the temperature of the body from 0.5° to 2° C. (0.9° to 3.6° F.), although the sensation of warmth is experienced.

Analytical reactions for ethyl alcohol.

1. Dissolve a small crystal of iodine in about 2 c c. of alcohol; add to the cold solution potassium hydroxide until the brown color of the solution disappears; a yellow precipitate of iodoform, CHI_3, forms. Many other alcohols, aldehyde, acetone, etc., show the same reaction.

2. Add to about 1 c.c. of alcohol the same volume of sulphuric acid; heat to boiling and add gradually a little more alcohol: the odor of ethyl ether will be noticed distinctly on further heating.

3. Add to a mixture of equal volumes of alcohol and sulphuric acid, a crystal (or strong solution) of sodium acetate: acetic ether is formed and recognized by its odor.

4. To about 2 c.c. of potassium dichromate solution add 0.5 c.c. of sulphuric acid and 1 c c. of alcohol: upon heating gently the liquid becomes green from the formation of chromic sulphate, while aldehyde is formed and may be recognized by its odor.

Alcoholic liquors. Numerous substances containing sugar or starch (which may be converted into sugar) are used in the manufacture of the various alcoholic liquors, all of which contain more or less of ethyl alcohol, besides coloring matter, ethers, compound ethers, and many other substances.

White and *red wines* are obtained by the fermentation of the grape-juice; the so-called *light wines* contain from 10 to 12, the *strong wines*, such as *port* and *sherry*, from 19 to 25 per cent. of alcohol; if the grapes contain much sugar, only a portion of it is converted into alcohol, whilst another portion is left undecomposed; such wines are known as *sweet wines. Effervescent wines*, as champagne, are bottled before the fermentation is complete; the carbonic acid is disengaged under pressure and retained in solution in the liquid.

Beer is prepared by fermentation of germinated grain (generally barley) to which much water and some hops have been added; the active principle of hops is *lupulin*, which confers on the beer a pleasant, bitter flavor, and the property of keeping without injury. *Light beers* have from 2 to 4, *strong beers*, as *porter* or *stout*, from 4 to 6 per cent. of alcohol.

Spirits differ from either wines or beers in so far as the latter are not distilled, and therefore contain also non-volatile organic and inorganic substances, such as salts, etc., not found in the spirits, which are distilled liquids containing volatile compounds only. Moreover, the quantity of alcohol in spirits is very much larger, and varies from 45 to 55 per cent. Of distilled spirits may be mentioned: *American whiskey,* made from fermented rye or Indian corn; *Irish whiskey,* from potatoes; *Scotch whiskey,* from barley; *brandy* or *cognac,* by distilling French wines; *rum,* by fermenting and distilling molasses; *arrack,* from fermented rice; *gin,* from various grains flavored with juniper berries.

Amyl alcohol, $C_5H_{11}OH$. This alcohol is frequently formed in small quantities during the fermentation of corn, potatoes, and other substances. When the alcoholic liquors are distilled, amyl alcohol passes over toward the end of the distillation, generally accompanied by propyl, butyl, and other alcohols, and by certain ethers and compound ethers. A mixture of these substances is known as *fusel oil,* and, from this liquid, amyl alcohol may be obtained in a pure state. It is an oily, colorless liquid, having a peculiar odor, and a burning, acrid taste; it is soluble in alcohol, but not in water. By oxidation of amyl alcohol, valerianic acid is obtained.

Amylene hydrate, Ethyl-dimethyl-carbinol, $C_5H_{12}O$, is an alcohol isomeric with the above amyl alcohol, but yielding only acetic acid on oxidation. It is a colorless liquid, having a pungent, ethereal odor, and a boiling-point of 100° C. (212° F.).

Glycerin, Glycerinum, $C_3H_5(OH)_3$ (*Glycerol*). Glycerin is the triatomic or tri-acid alcohol of the residue glyceryl, C_3H_5, formed by removal of the three atoms of hydrogen from the saturated hydrocarbon propane, C_3H_8, and by combination of the residue with 3OH.

Glycerin is a normal constituent of all fats, which are glycerin in which the three atoms of hydrogen of the hydroxyl have been replaced by radicals of fat acids. When fats are treated with alkalies, these latter combine with the fat acids, whilst glycerin is liberated. Upon this decomposition, carried out on a large scale in the manufacture of soap, depends the mode of obtaining glycerin.

Pure glycerin is a clear, colorless, odorless liquid of a syrupy consistence, oily to the touch, hygroscopic, very sweet, and neutral in reaction, soluble in water and alcohol in all proportions, but insoluble in ether, chloroform, benzol, and fixed oils; its specific gravity is 1.255; it cannot be distilled by itself without decomposition, but is volatilized in the presence of water, or when hot steam is allowed to pass through it.

Glycerin is a good solvent for a large number of organic and inorganic substances; the solutions thereby obtained are often termed *glycerites;* official are the glycerites of starch, carbolic acid, tannic acid, and a few others.

Boroglycerin is made by heating a mixture of boric acid and glycerin, when the compound $C_3H_5BO_3$ is obtained.

Analytical reactions.

1. A borax bead immersed for a few minutes in a solution of glycerin (made slightly alkaline with potassium hydroxide) imparts a green color to a non-luminous flame, owing to the liberation of boric acid.

2. Glycerin slightly warmed with an equal volume of sulphuric acid should not turn dark, but, on further heating, the characteristic, irritating odor of acroleïn is noticed.

3. Fehling's solution (see index) should not cause a red precipitation on heating, indicating the absence of glucose and dextrin.

Nitro-glycerin, $C_3H_5(NO_3)_3$ (*Glyceryl tri-nitrate, Glonoin*). When glycerin is treated with nitric acid, or, better, with a mixture of concentrated sulphuric and nitric acids, chemical action takes place resulting in the formation of glyceryl mono-nitrate, or tri-nitrate, substances belonging to the group of compound ethers, the constitution of which will be explained later.

$$C_3H_5(OH)_3 + 3HNO_3 = C_3H_5(NO_3)_3 + 3H_2O.$$

The tri-nitro-glycerin is the common nitro-glycerin, a pale-yellow oily liquid, which is nearly insoluble in water, soluble in alcohol, crystallizes at —20° C. (—4° F.) in long needles, and explodes very violently by concussion; it may be burned in an open vessel, but explodes when heated over 250° C. (482° F.).

Spirit of glonoin is an alcoholic solution of nitro-glycerin, containing of this substance 1 per cent.

Dynamite is infusorial earth impregnated with nitro-glycerin.

Phenols. The substances termed phenols are formed by replacement of hydrogen by hydroxyl in the aromatic hydrocarbons of the benzene series; they have the constitution of alcohols, but are not alcohols in the sense in which this term is used. The more important substances belonging to this group will be considered later.

QUESTIONS.—401. What is the general constitution of alcohols, and what is the difference between monatomic, diatomic, and triatomic alcohols? 402. How do alcohols occur in nature? 403. By what processes may alcohols be formed artificially, and how may they be separated from their combinations? 404. State the general properties of alcohols. 405. Mention names and composition of the first five members of alcohols of the general composition $C_nH_{2n+1}OH$.

42. ALDEHYDES. HALOID DERIVATIVES.

Aldehydes. The name aldehyde is derived from alcohol dehydrogenatum, referring to its method of formation, viz., by the removal of hydrogen from alcohols, as, for instance:

$$\underset{\text{Ethyl alcohol.}}{C_2H_6O} - 2H = \underset{\text{Acetic aldehyde.}}{C_2H_4O}.$$

This removal of hydrogen may be accomplished by various methods, as, for instance, by oxidation of alcohols, when one atom of oxygen combines with two atoms of hydrogen, forming water, whilst an aldehyde is formed at the same time. Aldehydes, when further oxidized, are converted into acids; aldehydes are, consequently, the intermediate products between alcohols and acids, and are frequently looked upon as the hydrides of the acid radicals. The constitution of acetic acid may be represented by the formula $CH_3.CO.OH$; the radical of acetic acid or acetyl is the group $CH_3.CO$, and the hydride of acetyl is acetic aldehyde, $CH_3.COH$. It is the group COH which is characteristic of, and found in, all aldehydes. Only a few aldehydes are of practical interest, as, for instance, acetic aldehyde, paraldehyde, and benzoic aldehyde, which latter substance will be more fully considered in connection with the aromatic substances.

Acetic aldehyde, C_2H_4O or CH_3COH. Alcohol may be converted into aldehyde by the action of various oxidizing agents; the one generally used is potassium dichromate, which oxidizes two hydrogen atoms of the alcohol molecule, converting it into aldehyde:

$$C_2H_6O + O = C_2H_4O + H_2O.$$

Experiment 44. Place in a 500 c.c. flask, provided with a funnel-tube and connected with a Liebig's condenser, 6 grammes of potassium dichromate. Pour upon this salt through the funnel-tube, very slowly, a previously prepared and cooled mixture of 5 c.c. of sulphuric acid, 24 c c. of water and 6 c.c. of alcohol. Chemical action begins generally without application of heat, and often becomes so violent that the liquid boils up, for which reason a large flask is used. The escaping vapors, which are a mixture of aldehyde, alcohol, and water, are collected in a receiver kept cold by ice. From this mixture pure

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406. By what process is methyl alcohol obtained, under what other names is it known, and what are its properties? 407. Describe the manufacture of pure alcohol from sugar. 408. Give the alcoholic strength of the alcohol and diluted alcohol of the U. S. P., and also of spirit of wine, proof-spirit, light wines, heavy wines, beers, and spirits. 409. What are the general properties of common alcohol? 410. What is glycerin, how is it found in nature, how is it obtained, and what are its properties?

aldehyde may be obtained by repeated distillation. Use the distillate for silvering a test-tube by adding some ammoniated silver nitrate. How much potassium dichromate is needed for the conversion of 5 grammes of pure alcohol into aldehyde?

Aldehyde is a neutral, colorless liquid, having a strong and characteristic odor; it mixes with water and alcohol in all proportions and boils at 21° C. (69.8° F.). The most characteristic chemical property of aldehyde is its tendency to combine *directly* with a great number of substances; thus it combines with hydrogen to form alcohol, with oxygen to form acetic acid, with ammonia to form *aldehyde-ammonia*, $C_2H_4O.NH_3$, a beautifully crystallizing substance, with hydrocyanic acid to form *aldehyde hydrocyanide*, $C_2H_4O.HCN$, and with many other substances. In the absence of such other substance it unites often with itself, forming polymeric modifications, such as paraldehyde and metaldehyde.

Aldehyde is a strong reducing agent, which property is used in the silvering of glass, which is done by adding aldehyde to an ammoniacal solution of silver nitrate, when metallic silver is deposited on the walls of the vessel or upon substances immersed in the solution.

Paraldehyde, $C_6H_{12}O_3$. When a few drops of concentrated sulphuric acid are added to aldehyde, this becomes hot and solidifies on cooling to 0° C. (32° F.). This solid crystalline mass of paraldehyde, which liquefies at 10.5° C. (51° F.), has been formed by the direct union of three molecules of common aldehyde. Paraldehyde is soluble in 8.5 parts of water, boils at 124° C. (253° F.), and is reconverted into common aldehyde by boiling it with dilute sulphuric or hydrochloric acid.

Metaldehyde, $(C_2H_4O)x$, is another polymeric modification of aldehyde, obtained by a process similar to the one mentioned for paraldehyde, but at a lower temperature. It is a solid crystalline substance, insoluble in water, but slightly soluble in alcohol, ether, and chloroform.

Trichloraldehyde, Chloral, C_2HCl_3O or $CCl_3.COH$ (*Trichloracetyl hydride*). This substance may be looked upon as acetic aldehyde, C_2H_4O, in which three atoms of hydrogen have been replaced by chlorine. It is made by passing a rapid stream of dry chlorine into pure alcohol to saturation, keeping the alcohol cool during the first few hours, and warming it gradually until the boiling-point is reached. According to the quantity of alcohol operated on, the conversion requires several hours or even days. The crude liquid product separates into two layers; the lower is removed and shaken with three times its volume of strong sulphuric acid and distilled, the distillate is mixed with calcium oxide and again distilled; the portion passing over between 94° and 99° C. (201° and 210° F.) is collected.

The decomposition taking place between alcohol and chlorine may be explained by the formation of aldehyde:

$$C_2H_6O + 2Cl = C_2H_4O + 2HCl,$$

and by the subsequent replacement of hydrogen by chlorine:

$$C_2H_4O + 6Cl = C_2HCl_3O + 3HCl$$

The actual decomposition is, however, somewhat more complicated, numerous other products being formed at the same time. By treatment with sulphuric acid these other substances are removed.

Chloral is a colorless, oily liquid, having a penetrating odor and an acrid, caustic taste; its specific gravity is 1.5, and its B. P. 95° C. (202° F.).

Chloral hydrate, Chloral, U. S. P., $C_2HCl_3O.H_2O$=165.2. When water is added to chloral the two substances combine, heat is disengaged, and the hydrate of chloral is formed, which is a crystalline, colorless substance, having an aromatic, penetrating odor, a bitter, caustic taste, and a neutral reaction; it is freely soluble in water, alcohol, and ether, also soluble in chloroform, carbon disulphide, benzene, fatty and essential oils, etc.; it liquefies when mixed with carbolic acid or with camphor; it melts at 58° C. (136° F.), and boils at 95° C. (203° F.), and also volatilizes slowly at ordinary temperature.

Chloral, and its hydrate, are decomposed by weak alkalies into chloroform and a formate of the alkali metal:

$$\underset{\text{Chloral.}}{C_2HCl_3O} + \underset{\text{Potassium hydroxide.}}{KHO} = \underset{\text{Potassium formate.}}{KCHO_2} + \underset{\text{Chloroform.}}{CHCl_3}.$$

This decomposition was believed to take place in the animal body, and especially in the blood, whenever chloral was given internally, but recent investigations seem to contradict this assumption. There is no chemical antidote which may be used in cases of poisoning by chloral, and the treatment is, therefore, confined to the use of the stomach-pump and to the maintenance of respiration.

Analytical reactions for chloral.

1. Chloral or chloral hydrate heated with potassium hydroxide is converted into potassium formate and chloroform, which latter may be recognized by its odor. (See explanation above.)

2. Heated with silver nitrate and ammonium hydroxide a silver-mirror is formed on the glass.

3. Heated with Fehling's solution a red precipitate is formed.

See also reactions 2 and 6 for chloroform below.

Chloroform, Chloroformum, $CHCl_3 = 119.2$ (*Trichlormethane, Dichlormethyl chloride*). When either chlorine, bromine, or iodine is allowed to act upon methane, CH_4, a number of substitution products are formed. Thus, if methane is considered as methyl hydride, CH_3H, the first product of substitution is methyl chloride, CH_3Cl; the second is monochlormethyl chloride, CH_2ClCl; the third is dichlormethyl chloride or chloroform, $CHCl_2Cl$; and the fourth is carbon tetrachloride, CCl_4. Similar products are formed by the action of iodine or bromine upon methane, or, in fact, upon any of the paraffins.

Chloroform is, however, not obtained for commerce by the above process, but by the action of bleaching-powder and calcium hydroxide on alcohol. The three substances named, after being mixed with a considerable quantity of water, are heated in a retort until distillation commences; the crude product of distillation is an impure chloroform, which is purified by mixing it with strong sulphuric acid and allowing the mixture to stand; the upper layer of chloroform is removed and treated with sodium carbonate (to remove any acids) and distilled over calcium oxide (to remove water).

The explanation of the formation of chloroform by the above process has indirectly been given in connection with the consideration of chloral, where it has been shown that alcohol is converted by the action of chlorine first into aldehyde and subsequently into chloral, which, upon being treated with alkalies, is decomposed into an alkali formate and chloroform.

The action of the chlorine of the calcium hypochlorite (which is the active principle in bleaching-powder) upon the alcohol is similar to that of free chlorine upon alcohol; in both cases aldehyde, and afterward chloral, are formed, which latter, in the manufacture of chloroform, is decomposed by the calcium hydroxide into chloroform and calcium formate. The last-named salt is, however, not found in the residue of the distillation, because it is decomposed by bleaching-powder and calcium hydroxide into calcium carbonate, chloride, and water:

$$Ca(CHO_2)_2 + Ca(ClO)_2 + Ca(OH)_2 = 2CaCO_3 + CaCl_2 + 2H_2O.$$

If the various intermediate steps of the decomposition are not considered, the process may be represented by the following equation:

$$\underset{\text{Alcohol.}}{4C_2H_6O} + \underset{\text{Calcium hypochlorite.}}{8Ca(ClO)_2} = \underset{\text{Chloroform.}}{2CHCl_3} + \underset{\text{Calcium formate.}}{3[Ca(CHO_2)_2]} + \underset{\text{Calcium chloride.}}{5CaCl_2} + \underset{\text{Water.}}{8H_2O}.$$

Chloroform is now made extensively by the action of bleaching-powder upon acetone; the reaction takes place thus:

$$\underset{\text{Acetone.}}{2CO(CH_3)_2} + \underset{\substack{\text{Calcium}\\\text{hypochlorite.}}}{3Ca(ClO)_2} = \underset{\text{Chloroform.}}{2CHCl_3} + \underset{\substack{\text{Calcium}\\\text{hydroxide.}}}{2Ca(OH)_2} + \underset{\substack{\text{Calcium}\\\text{acetate.}}}{Ca(C_2H_3O_2)_2}.$$

Pure chloroform is a heavy, colorless liquid, of a characteristic ethereal odor, a burning, sweet taste, and a neutral reaction; it is but very sparingly soluble in water, but miscible with alcohol and ether in all proportions; the specific gravity of pure chloroform is 1.50, but a small quantity of alcohol (from one-half to one per cent.), allowed to be present by the U. S. P., causes the specific gravity to be about 1.488; boiling-point 62° C. (143° F.), but rapid evaporation takes place at all temperatures.

Chloroform should be tested for excess of alcohol by specific gravity; for hydrochloric acid and chlorine by shaking it with water, which afterward should not give a precipitate with silver nitrate; for aldehyde by heating with solution of potassium hydroxide, which should not be colored brown; for empyreumatic and other organic compounds by shaking with an equal volume of pure sulphuric acid, which should remain colorless; or by evaporation, when no residue should be left and no odor should be perceptible after the chloroform has been volatilized.

Analytical reactions for chloroform.

1. Dip a strip of paper into chloroform and ignite. The flame has a green mantle and emits vapors of hydrochloric acid, rendered more visible upon the approach of a glass rod moistened with water of ammonia.

2. Add a drop of chloroform and a drop of aniline to some alcoholic solution of potassium hydroxide and heat gently: a peculiar, penetrating, offensive odor of benzo-isonitril, C_6H_5NC, is noticed. (Chloral shows the same reaction.)

$$CHCl_3 + 3KOH + C_6H_5.NH_2 = C_6H_5NC + 3KCl + 3H_2O.$$

3. Add some chloroform to Fehling's solution and heat: red cuprous oxide is precipitated.

4. Vapors of chloroform, when passed through a glass tube heated to redness, are decomposed into carbon, chlorine, and hydrochloric acid. The two latter should be passed into water, and may be recognized by their action on silver nitrate (white precipitate of silver nitrate) and on mucilage of starch, to which potassium iodide has been added (blue iodized starch is formed).

5. Heat some chloroform with solution of potassium hydroxide and a little alcohol. Chloroform is decomposed into potassium chloride and formate:

$$CHCl_3 + 4KOH = 3KCl + KCHO_2 + 2H_2O.$$

Divide solution into two portions. Acidulate one portion with nitric acid, boil, and add silver nitrate: white precipitate of silver nitrate. To second portion add a little water of ammonia and a crystal of silver nitrate: a mirror of metallic silver will be formed after heating slightly.

6. Add to 1 c.c. of chloroform about 0.3 gramme of resorcin in solution, and 3 drops of solution of sodium hydroxide; boil strongly: a yellowish-red color is produced, and the liquid shows a beautiful yellow-green fluorescence. (Chloral shows the same reaction.)

In cases of poisoning chloroform is generally to be sought for in the lungs and blood, which are placed in a flask connected with a tube of difficultly fusible glass. By heating the flask the chloroform is expelled and decomposed in the heated glass tube, as stated above in reaction 4. Another portion of chloroform should be distilled without decomposing it, and the distillate tested as above stated.

What has been said above regarding antidotes to chloral holds good for chloroform also.

Bromoform, $CHBr_3$ (*Dibromomethyl bromide*). Obtained by gradually adding bromine to a cold solution of potassium hydroxide in methyl alcohol until the color is no longer discharged, and rectifying over calcium chloride.

Bromoform is a colorless liquid which has an aromatic odor and a sweet taste. Sp. gr. 2.9; B. P. 150°C. (302° F.); solidifies at —9° C. (158° F.). It is sparingly soluble in water, soluble in alcohol and ether. Its physiological action is similar to that of chloroform.

Iodoform, Iodoformum, CHI_3 = 292.6 (*Diiodomethyl iodide*). This compound is analogous in its constitution to chloroform and bromoform. It is made by heating together an aqueous solution of an alkali carbonate, iodine, and alcohol until the brown color of iodine has disappeared; on cooling, iodoform is deposited in yellow scales, which are well washed with water and dried between filtering paper. (For an explanation of the chemical changes taking place see above, under chloral and chloroform.)

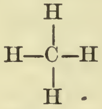
Iodoform occcurs in small, lemon-yellow, lustrous crystals, having a peculiar, penetrating odor, and an unpleasant, sweetish taste; it is nearly insoluble in water and acids, soluble in alcohol, ether, fatty and essential oils. It contains 96.7 per cent. of iodine.

Iodoform digested with an alcoholic solution of potassium hydroxide imparts, after acidulation with nitric acid, a blue color to starch solution.

Experiment 45. Dissolve 4 grammes of crystallized sodium carbonate in 6 c.c. of water: add to this solution 1 c.c. of alcohol; heat to about 70° C. (158° F.), and add gradually 1 gramme of iodine. A yellow crystalline deposit of iodoform separates.

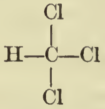
Ethyl bromide, C_2H_5Br (*Hydrobromic ether*). Obtained by the simultaneous action of phosphorus and bromine on ethyl alcohol. It is a colorless, ethereal liquid, which boils at 40° C. (104° F.) and has a sp. gr. of 1.473.

Sulphonal, $(CH_3)_2C(C_2H_5SO_2)_2$, *Dimethyl-diethylsulphonyl-methane.* It has been stated before that mercaptans are alcohols in which the oxygen is replaced by sulphur. Alcohol treated with oxidizing agents are converted into acids by exchanging two atoms of hydrogen for one atom of oxygen. Mercaptans behave differently; they combine directly with three atoms of oxygen, forming compounds known as *sulphonic acids.* Thus, ethyl mercaptan, C_2H_5HS, when treated with nitric acid, is converted into ethyl-sulphonic acid, $C_2H_5HSO_3$. The radical of this acid, known as ethylsulphonyl, $C_2H_5SO_2$, may, by indirect process, be caused to replace hydrogen in methane, CH_4, twice, while the two remaining methane hydrogen atoms can be replaced by methyl. The compound thus obtained is the dimethyl-diethylsulphonyl-methane, or sulphonal. The relations between methane and some of its derivatives, which have been considered in this chapter, may be shown graphically thus:



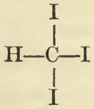
$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

Methane.



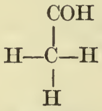
$$\begin{array}{c} Cl \\ | \\ H-C-Cl \\ | \\ Cl \end{array}$$

Chloroform.



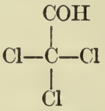
$$\begin{array}{c} I \\ | \\ H-C-I \\ | \\ I \end{array}$$

Iodoform.



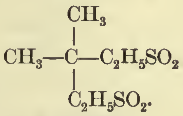
$$\begin{array}{c} COH \\ | \\ H-C-H \\ | \\ H \end{array}$$

Aldehyde.



$$\begin{array}{c} COH \\ | \\ Cl-C-Cl \\ | \\ Cl \end{array}$$

Chloral.



$$\begin{array}{rcl} & CH_3 & \\ & | & \\ CH_3- & C & -C_2H_5SO_2 \\ & | & \\ & C_2H_5SO_2. & \end{array}$$

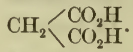
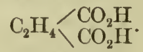
Sulphonal.

Sulphonal is a white crystalline substance, having neither odor nor taste; it is soluble in 15 parts of boiling and 500 parts of cold water, soluble with difficulty in alcohol; it fuses at 130° C. (266° F.), and volatilizes at about 300° C. (572° F.), with partial decomposition. A mixture of sulphonal with either wood charcoal or with potassium cyanide evolves, on heating, the characteristic odor of mercaptan.

QUESTIONS.—411. What is an aldehyde, and what are its relations to alcohols and acids? 412. State the composition of acetic aldehyde. 413. Explain the action of chlorine upon alcohol. 414. Give the composition and properties

43. MONOBASIC FATTY ACIDS.

General constitution of organic acids. When hydroxyl, OH, replaces hydrogen in hydrocarbons, alcohols are formed; when the univalent group, CO_2H, known as *carboxyl*, replaces hydrogen in hydrocarbons, acids are formed. Monatomic, diatomic, and triatomic alcohols are formed by introducing hydroxyl once, twice, or three times respectively into hydrocarbon molecules; monobasic, dibasic, and tribasic acids are formed by substituting one, two, or three hydrogen atoms by carboxyl. For instance:

Hydrocarbons.	*Monobasic acids.*	*Dibasic acids.*
CH_4	$CH_3 \cdot CO_2H$	 $CH_2\left<\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$.
Methane.	Acetic acid.	Malonic acid.
C_2H_6	$C_2H_5\ CO_2H$	 $C_2H_4\left<\begin{matrix}CO_2H\\CO_2H\end{matrix}\right.$.
Ethane.	Propionic acid.	Succinic acid.

The constitution of carboxyl is represented by $O{=}\overset{|}{C}{-}O{-}H$, which shows that of the four affinities of the carbon atom, two are saturated by an atom of oxygen, one by hydroxyl, whilst one is unprovided for; any univalent hydrocarbon residue may attach itself to this unprovided affinity, when an acid is formed. Acids may be looked upon, therefore, as being composed of hydrocarbon residues and hydroxyl, united by the bivalent radical CO, termed *carbonyl.* By replacement of the hydrogen of the hydroxyl (or of the carboxyl, which is the same) by metals the various salts are formed.

What is termed the *acid radical* is the group of the total number of atoms present in the molecule, with the exception of the hydroxyl. In acetic acid, $C_2H_4O_2$, for instance, the radical is CH_3CO, or C_2H_3O, which group of atoms, known as acetyl, is characteristic of acetic acid, and of all acetates, and may often be transferred from one compound into another without decomposition.

The difference between alcohol radicals and acid radicals may also be stated, by saying that the first contain carbon and hydrogen only, while acid radicals contain carbon, hydrogen, and oxygen.

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of chloral and chloral hydrate. 415. What decomposition takes place when alkalies act upon chloral? 416. Describe the process of preparing and purifying chloroform. 417. What is the composition of chloroform and what are its properties? 418. How is chloroform tested for impurities? 419. By what tests may chloroform be recognized? 420. How is iodoform made, and what are its properties?

In a similar manner, as there are homologous series of alcohols corresponding to the various series of hydrocarbons, there are also homologous series of organic acids running parallel with the corresponding series of hydrocarbons or alcohols.

Occurrence in nature. Organic acids are found and formed both in vegetables and animals, and are present either in the free state, or (and more generally) in combination with bases as salts, or with alcohols as compound ethers. Uncombined or as salts are found, for instance, citric, tartaric, and oxalic acids in plants, formic acid in some insects, uric acid in urine, etc.; as compound ethers are found many of the fatty acids in the various fats.

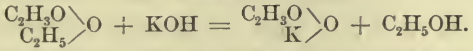
Some organic acids are also found as products of the decomposition of organic matters in nature.

Formation of acids. Many acids are produced by oxidation of alcohols. As intermediate products are formed aldehydes, which may be looked upon (as stated in the last chapter) as alcohols from which two atoms of hydrogen have been removed. For instance:

$$\underset{\text{Ethyl alcohol.}}{C_2H_5OH} + O = \underset{\text{Acetic aldehyde.}}{C_2H_3OH} + H_2O.$$

$$\underset{\text{Acetic aldehyde.}}{C_2H_3OH} + O = \underset{\text{Acetic acid.}}{C_2H_3O.OH.}$$

Acids are obtained from compound ethers by boiling them with alkalies, when salts are formed, which may be decomposed by sulphuric or other acids. For instance:



$$\underset{\text{Ethyl acetate.}}{\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right>O} + \underset{\substack{\text{Potassium}\\\text{hydroxide.}}}{KOH} = \underset{\substack{\text{Potassium}\\\text{acetate.}}}{\left.\begin{matrix}C_2H_3O\\K\end{matrix}\right>O} + \underset{\text{Ethyl alcohol.}}{C_2H_5OH.}$$

$$\underset{\substack{\text{Potassium}\\\text{acetate.}}}{2C_2H_3KO_2} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\text{Acetic acid.}}{2C_2H_4O_2} + \underset{\substack{\text{Potassium}\\\text{sulphate.}}}{K_2SO_4.}$$

Acids are formed also by destructive distillation (acetic acid); by fermentation (lactic acid); by putrefaction (butyric acid); by oxidation of many organic substances (oxalic acid by oxidation of starch), etc.

Properties. Organic acids show the characteristics mentioned of inorganic acids, viz., when soluble, have an acid or sour taste, redden litmus, and contain hydrogen replaceable by metals, with the formation of salts.

Most organic acids, and especially the higher members, show these acid properties in a less marked degree than inorganic acids; in fact, they become so weak that the acid properties can often scarcely be recognized. As stated above, mono-, di-, and tri-basic organic acids are known, the latter two being capable of forming normal, acid, or double salts.

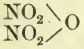
Most organic acids are colorless, some of the lower and volatile acids have a characteristic odor, but most of them are odorless; most organic acids are solids, some liquids, scarcely any gaseous at the ordinary temperature. Any salt formed by the union of an organic acid and a non-volatile metal (especially alkali metal) leaves the carbonate of this metal after the salt has suffered combustion. It is for this reason that ashes contain metals largely in the form of carbonates.

Whilst the hydrogen of the hydroxyl may be replaced by metals or by other residues, the hydrogen of the acid radical may often be replaced by chlorine, and the oxygen of the hydroxyl by sulphur. The acids formed by this last reaction are known as *thio acids*, for instance, thio-acetic acid, C_2H_4OS.

When the hydrogen of the hydroxyl is replaced by a second acid radical (of the same kind as the one forming the acid) the so-called *anhydrides* are produced, which correspond to the inorganic anhydrides. For instance:

HNO_3 or $NO_2.OH$

Nitric acid.

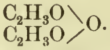


$$\begin{matrix} NO_2 \\ NO_2 \end{matrix}\!\!>\!O$$

Nitric anhydride.

$C_2H_4O_2$ or $C_2H_3O.OH$.

Acetic acid.



$$\begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\!\!>\!O.$$

Acetic andydride.

Amido-acids are compounds obtained from acids by replacement of a hydrogen atom by NH_2; these compounds will be spoken of later in connection with amides.

Fatty acids of the general composition,

$C_nH_{2n}O_2$ or $C_nH_{2n+1}CO_2H$.

		Fusing-point.	*Boiling-point.*	*Occurs in:*
Formic acid,	$H\ CO_2H$	+ 4° C.	100° C.	Red ants and some plants, etc.
Acetic acid,	$C\ H_3\ CO_2H$	+17	118	Vegetable and animal fluids.
Propionic acid,	$C_2\ H_5\ CO_2H$	—21	140	Sweat, fluids of the stomach, etc.
Butyric acid,	$C_3\ H_7\ CO_2H$	—20	162	Butter.
Valerianic acid,	$C_4\ H_9\ CO_2H$	—16	185	Valerian root.
Caproic acid,	$C_5\ H_{11}CO_2H$	— 2	205	Butter.
Œnanthylic acid,	$C_6\ H_{13}CO_2H$	—10	224	Castor oil.
Caprylic acid,	$C_7\ H_{15}CO_2H$	+14	236	Butter; cocoanut oil.
Pelargonic acid,	$C_8\ H_{17}CO_2H$	18	254	Leaves of geranium.
Capric acid,	$C_9\ H_{19}CO_2H$	30	270	Butter.
Lauric acid,	$C_{11}H_{23}CO_2H$	43	.....	Cocoanut oil.
Myristic acid,	$C_{13}H_{27}CO_2H$	54	.....	

		Fusing-point.	Boiling-point.	Occurs in :
Palmitic acid,	$C_{15}H_{31}CO_2H$	62	.....	Palm oil, butter.
Margaric acid,	$C_{16}H_{33}CO_2H$	60	.....	(Obtained artificially.)
Stearic acid,	$C_{17}H_{35}CO_2H$	70	.....	Most solid animal fats.
Arachidic acid,	$C_{19}H_{39}CO_2H$	75	.....	Oils of certain plants.
Behenic acid,	$C_{21}H_{43}CO_2H$	76	.....	
Hyænic acid,	$C_{24}H_{49}CO_2H$	77	.....	
Cerotic acid,	$C_{26}H_{53}CO_2H$	80	.....	Beeswax.
Melissic acid,	$C_{29}H_{59}CO_2H$	90	.....	

The name fatty acids has been given to these acids on account of their frequent occurrence in fats, and also in allusion to the somewhat fatty appearance of the higher members of the series.

The gradual change of properties which the members of an homologous series show, is well marked in the series of fatty acids, thus:

First member.	Last member.
Is liquid.	Is solid.
Volatilized at 100° C.	Not volatilized without decomposition.
Strongly acid.	Scarcely acid.
Strongly odoriferous.	Odorless.
Easily soluble in water.	Insoluble in water.
Produces no grease spot.	Produces a grease spot.
Forms salts easily soluble without decomposition.	Forms salts which are insoluble or decomposed by water.

The intermediate members of the series show intermediate properties, and this change in properties is in proportion to the gradual change in molecular weight.

Formic acid, $H.CO_2H$ or $CHO.OH$. This acid is found in the red ant and in other insects, which eject it when irritated. It is also contained in some plants, as, for instance, in the leaves of the stinging nettle.

It is formed by the oxidation of methyl alcohol :

$$\underset{\text{Methyl alcohol.}}{CH_3O} + O_2 = \underset{\text{Formic acid.}}{CH_2O_2} + H_2O,$$

by the action of carbonic oxide on potassium hydroxide :

$$KOH + CO = \underset{\text{Potassium formate.}}{KCHO_2},$$

by the action of potassium hydroxide on chloroform :

$$CHCl_3 + 4KOH = 3KCl + 2H_2O + KCHO_2,$$

by heating equal parts of glycerin and oxalic acid, when the latter is split up into carbon dioxide and formic acid, which may be separated from the glycerin by distillation :

$$\underset{\text{Oxalic acid.}}{C_2H_2O_4} = CO_2 + \underset{\text{Formic acid.}}{CH_2O_2}.$$

It is also a product of the decomposition of sugar, starch, etc. Formic acid is a colorless liquid having a penetrating odor, and a strongly acid taste; it produces blisters on the skin; it is a powerful deoxidizer, being, when thus acting, converted into carbon dioxide and water:

$$CH_2O_2 + O = CO_2 + H_2O.$$

Acetic acid, $H.C_2H_3O_2$, or $C_2H_3O.OH$, or $CH_3.CO_2H = 60$. The most important alcohol is ethyl alcohol, and the most largely used organic acid is acetic acid, obtained from ethyl alcohol by oxidation. Acetic acid is found in combination with alkali metals in the juices of many plants, also in the secretions of the glands, etc.

Acetic acid is formed chiefly either by the oxidation of alcohol (and aldehyde) or by the destructive distillation of wood. It is produced commercially on a large scale as follows: A diluted alcohol (8 to 10 per cent.) is allowed to trickle down slowly through wood-shavings contained in high casks having perforated sides in order to allow a free circulation of the air; the temperature is kept at about 24° to 30° C. (75° to 86° F.), and the liquid having passed through the shavings is repeatedly poured back in order to cause complete oxidation. When the latter object has been accomplished the liquid is a diluted acetic acid.

It appears that the conversion of alcohol into acetic acid is greatly facilitated by the presence of a microscopic organism (mycoderma aceti) commonly termed "mother of vinegar." This serves in some unexplained way to convey the atmospheric oxygen to the alcohol. The term "acetic fermentation" is often applied to this conversion, although it is not a true fermentation, since no splitting up of the alcohol molecule into other less complex compounds, but a process of slow oxidation, takes place.

The second process for manufacturing acetic acid is the heating of wood to a red heat in iron retorts, when numerous products (gases, aqueous and tarry substances) are formed. The aqueous products contain, besides other substances, methyl alcohol and acetic acid. The liquid is neutralized with calcium hydroxide and distilled, when methyl alcohol, water, etc., evaporate and a solid residue is left, which is an impure calcium acetate. From this latter, acetic acid is obtained by distilling with sulphuric (or hydrochloric) acid, calcium sulphate (or chloride) being formed and left in the retort, whilst acetic acid distils over.

Experiment 46. Add to 54 grammes of sodium acetate contained in a small flask which is connected with a Liebig's condenser, 40 grammes of sulphuric acid. Apply heat and distil over about 35 c.c. Determine volumetrically the amount of pure acetic acid in this liquid.

Pure acetic acid, or *glacial acetic acid,* is solid at or below 15° C. (59° F.); at higher temperatures it is a colorless liquid having a characteristic, penetrating odor, boiling at 118° C. (224° F.), and causing blisters on the skin; its specific gravity is 1.056; it is miscible with water, alcohol, and ether, is strongly acid, forming salts known as acetates, which are all soluble in water.

Vinegar is dilute acetic acid (about 6 per cent.), containing often other substances, such as coloring matter, compound ethers, etc. Vinegar was formerly obtained exclusively by the oxidation of fermented fruit-juices (wine, cider, etc.), the various substances present in them imparting a pleasant taste and odor to the vinegar; to-day vinegar is often made artificially by adding various coloring and odoriferous substances to dilute acetic acid. Vinegar should be tested for sulphuric and hydrochloric acids, which are sometimes fraudulently added.

Acidum aceticum, Acidum aceticum dilutum, and *Acidum aceticum glaciale* are the three official forms of acetic acid. The first-named acid contains 36 per cent., the second 6 per cent., the third at least 99 per cent. of pure acetic acid.

Acetic acid shows an exceptional behavior in regard to the specific gravity of its aqueous solutions. The highest specific gravity of 1.0748 belongs to an acid of 78 per cent., which is equal to an acid containing one molecule of water and one of acetic acid, or $C_2H_4O_2.H_2O$. The addition of either acetic acid or of water causes the liquid to become lighter. For instance, the specific gravity of an acid containing 95 per cent. is equal to that containing 56 per cent. of pure acid, both solutions having a specific gravity of 1.066.

The specific gravity of dilute acetic acid cannot, therefore, be used as a means of determining the amount of pure acid; this is done by exactly neutralizing a weighed portion of the acid with an alkali; from the quantity of the latter used, the quantity of actual acid present may be easily calculated. (See also volumetric methods in Chapter 37.)

Analytical reactions.

(Sodium acetate, $NaC_2H_3O_2$, may be used.)

1. Any acetate heated with sulphuric acid evolves acetic acid, which may be recognized by its odor.

2. Acetic acids or acetates heated with sulphuric acid and alcohol give a characteristic odor of acetic ether.

3. A solution containing acetic acid, or an acetate carefully neutralized, turns deep red on the addition of solution of ferric chloride, and forms, on boiling, a reddish-brown precipitate of an oxyacetate of iron.

Potassium acetate, Potassii acetas, $KC_2H_3O_2 = 98$. Sodium acetate, Sodii acetas, $NaC_2H_3O_2.3H_2O = 136$. Zinc acetate, Zinci acetas, $Zn\ (C_2H_3O_2)_2.2H_2O = 219$. These three salts may be obtained by neutralizing the respective carbonates with acetic acid and evaporating the solution; they are white salts, easily soluble in water.

Ammonium acetate, $NH_4C_2H_3O_2$, is official in the form of a 7 per cent. solution, which is known as *Spirit of Mindererus.*

Ferric acetate, $Fe_2(C_2H_3O_2)_6$. A 33 per cent. solution of this salt is the *Liquor ferri acetatis* of the U. S. P. It is made by dissolving freshly precipitated ferric hydroxide in acetic acid; it is a dark, red-brown, transparent liquid of a specific gravity of 1.16.

Lead acetate, Plumbi acetas, $Pb(C_2H_3O_2)_23H_2O = 378.4$ (*Sugar of lead*), is made by dissolving lead oxide in diluted acetic acid. It forms colorless, shining, transparent crystals, easily soluble in water; on heating, it melts and then loses water of crystallization; at yet higher temperatures it is decomposed; it has a sweetish, astringent, afterward metallic taste. Commercial sugar of lead contains often an excess of lead oxide in the form of basic salts; such an article when dissolved in spring water gives generally a turbid solution, in consequence of the formation of lead carbonate; the addition of a few drops of acetic acid renders the liquid clear by dissolving the precipitate.

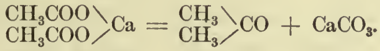
When a mixture of lead acetate and lead oxide is digested or boiled with water, the acetate combines with the oxide, forming a *basic lead acetate,* approximately $Pb(C_2H_3O_2)_2.PbO$, a 25 per cent. solution of which is the *Liquor plumbi subacetatis,* or *Goulard's extract,* whilst a solution containing about 1 per cent. is the *Liquor plumbi subacetatis dilutus,* or *lead-water.*

Cupric acetate, $Cu(C_2H_3O_2)_2H_2O$. The commercial *verdigris* is a basic acetate of copper, $Cu(C_2H_3O_2)_2CuO$, made by the action of dilute acetic acid and atmospheric air on metallic copper. By adding to this basic acetate more acetic acid, the neutral acetate is obtained, but this may be made directly also by dissolving cupric hydroxide or carbonate in acetic acid. It forms deep green, prismatic crystals, which are soluble in water.

By boiling verdigris with arsenous oxide, *cupric aceto-arsenite,* $3CuAs_2O_4 + Cu(C_2H_3O_2)_2$, is formed, which is the chief constituent of *emerald green* or *Schweinfurt green,* a substance often used as a coloring matter. *Paris green* is of a similar composition, but less pure.

Chlor-acetic acids. By treating acetic acid with chlorine, either one, two, or three hydrogen atoms may be replaced by this element, when either mono-, di-, or tri-chlor-acetic acid is formed. *Trichlor-acetic acid,* $C_2Cl_3HO_2$, is a colorless, crystalline substance, which fuses at 55° (131° F.), and boils at 195° C. (383° F.).

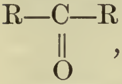
Acetone, C_3H_6O (*Dimethyl-ketone*). This compound is obtained by the destructive distillation of acetates (and of a number of other substances). The decomposition which calcium acetate suffers may be shown by the equation:



$$\begin{matrix}CH_3COO\diagdown\\CH_3COO\diagup\end{matrix}Ca = \begin{matrix}CH_3\diagdown\\CH_3\diagup\end{matrix}CO + CaCO_3.$$

Calcium acetate. Acetone.

The above graphic formula of acetone shows this substance to be dimethyl carbonyl, or carbon monoxide whose two available affinities have been satisfied by two methyl groups. Acetone is the representative of a series of compounds known as *acetones* or generally as *ketones,* the general composition of which may be assumed to be



$\underset{\underset{\displaystyle O}{\|}}{R-C-R}$, R representing in this case any univalent radical.

Acetone is a colorless liquid, boiling at 58° C. (136° F.), miscible with water, alcohol, and ether in all proportions; it has a peculiar ethereal, somewhat mint-like odor.

Butyric acid, $HC_4H_7O_2$. Among the glycerides of butter those of butyric acid are found; they exist also in cod-liver oil, croton oil, and a few other fatty oils; some volatile oils contain compound ethers of butyric acid; free butyric acid occurs in sweat and in cheese. It may be obtained by a peculiar fermentation of lactic acid (which itself is a product of fermentation), and is also generated during the putrefaction of albuminous substances. Butyric acid is a colorless liquid, having a characteristic, unpleasant odor; it mixes with water in all proportions.

Valerianic acid, $HC_5H_9O_2$ (*Valeric acid*). This acid occurs in valerian root and angelica root, from which it may be separated; it is, however, generally obtained by oxidation of amyl alcohol by potassium dichromate and sulphuric acid. After oxidation has taken place the mixture is distilled, when valerianic acid with some valerianate of amyl distils over. The change of amyl alcohol into valerianic acid is analogous to the conversion of ethyl alcohol into acetic acid :

$$\underset{\text{Amyl alcohol.}}{C_5H_{11}OH} + 2O = \underset{\text{Valerianic acid.}}{HC_5H_9O_2} + H_2O.$$

Pure valerianic acid is an oily, colorless liquid, having a penetrating, highly characteristic odor; it is slightly soluble in water, but soluble in alcohol ; it boils at 185° C. (365° F.).

Several of the salts of valerianic acid are official; they are the *valerianate of iron, of ammonium, of zinc,* and *of quinine.* The last named three compounds are white salts, while the ferric valerianate has a dark-red color ; the ammonium salt is easily soluble in water, the other three compounds are insoluble or nearly so.

Oleic acid, Acidum oleicum, $HC_{18}H_{33}O_2 = 282$. As shown by its formula, oleic acid does not belong to the above-described series of fatty acids of the composition $C_nH_{2n}O_2$, but to a series having the general composition $C_nH_{2n-2}O_2$.

Oleic acid is a constituent of most fats, especially of fat oils. Thus, olive oil is mainly oleate of glyceril. By boiling olive oil with potassium hydroxide, potassium oleate is formed, which may be decomposed by tartaric acid, when oleic acid is liberated.

Oleic acid is a nearly colorless, yellowish, or brownish-yellow, odorless, tasteless, neutral oily liquid, insoluble in water, soluble in alcohol, chloroform, oil of turpentine, and fat oils, crystallizing near the freezing-point of water; exposed to the air it decomposes and shows then an acid reaction. Lead oleate is soluble in ether, lead palmitate and lead stearate are not.

The official *oleates of mercury, zinc,* and *veratrine* are obtained by dissolving the yellow mercuric oxide, zinc oxide, or veratrine in oleic acid.

QUESTIONS.—421. What is the constitution of organic acids, which group of atoms is found in all of them, and how does an alcohol radical differ from an acid radical? 422. Give some processes by which organic acids are formed in nature or artificially. 423. Mention the general properties of organic acids. 424. Which series of acids is known as fatty acids, and why has this name been given to them? 425. Mention names, composition, and occurrence in nature of the first five members of the series of fatty acids. 426. By what

44. DIBASIC AND TRIBASIC ORGANIC ACIDS.

Dibasic acids of the general composition $C_nH_{2n-2}O_4$.

Oxalic acid	$H_2C_2O_4$ or	$(CO_2H)_2$.
Malonic acid	$H_2C_3H_2O_4$ or	$C\,H_2(CO_2H)_2$.
Succinic acid	$H_2C_4H_4O_4$ or	$C_2H_4(CO_2H)_2$.
Pyrotartaric acid	$H_2C_5H_6O_4$ or	$C_3H_6(CO_2H)_2$.
Adipic acid	$H_2C_6H_8O_4$ or	$C_4H_8(CO_2H)_2$.
etc.		

Of these acids, only the first member is of general interest.

Oxalic acid, $H_2C_2O_4.2H_2O$. This acid may be looked upon as a direct combination of two carboxyl groups, $CO_2H—CO_2H$, both atoms of hydrogen being replaceable by metals.

Oxalic acid is distributed largely in the vegetable kingdom in the form of potassium, sodium, or calcium salts. It may be obtained from vegetables, or by the oxidation of many organic substances, chiefly fats, sugars, starch, etc., by nitric acid or other strong oxidizing agents.

Experiment 74. Pour a mixture of 15 c.c. nitric acid and 35 c.c. of water upon 10 grammes of sugar contained in a 200 c.c. flask. Apply heat gently until the reaction begins. When red fumes cease to escape pour the solution into a porcelain dish and evaporate to about one-half its volume. Crystals of oxalic acid separate on cooling; use them for making the analytical reactions mentioned below.

Oxalic acid is manufactured on the large scale by heating sawdust with potassium or sodium hydroxide to about 250° C. (482° F.), when the oxalate of these metals is formed; by the addition of calcium hydroxide to the dissolved alkali oxalate, insoluble calcium oxalate is formed which is decomposed by sulphuric acid.

Oxalic acid crystallizes in large, transparent, colorless prisms, containing two molecules of water; it is soluble in water and alcohol, and has poisonous properties. When heated slowly, it sublimes at a

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processes may formic acid be obtained, and what are its properties? 427. Describe the processes of manufacturing acetic acid from alcohol and from wood. 428. What is vinegar, and what is glacial acetic acid? Give tests for acetic acid and for acetates. 429. Describe the processes for making the acetates of potassium, zinc, iron, lead, and copper, and also of Goulard's extract and lead-water; state their composition and properties. 430. When and in what form of combination is oleic acid found in nature, and what are its properties?

temperature of about 155° C. (311° F.); but if heated higher or with sulphuric acid it is decomposed into water, carbonic oxide, and carbon dioxide:

$$H_2C_2O_4 = H_2O + CO + CO_2.$$

Oxalic acid acts as a reducing agent, decolorizing solutions of the permanganates, and precipitating gold and platinum from their solutions:

$$PtCl_4 + 2H_2C_2O_4 = Pt + 4CO_2 + 4HCl.$$

Analytical reactions.

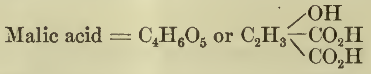
(Sodium oxalate, $Na_2C_2O_4$, may be used.)

1. Oxalic acid or oxalates when heated with strong sulphuric acid evolve carbonic oxide and carbon dioxide (see above).
2. Neutral solutions of oxalic acid give with calcium chloride a white precipitate of calcium oxalate, CaC_2O_4, which is insoluble in acetic, soluble in hydrochloric acid.
3. Silver nitrate produces a white precipitate of silver oxalate, $Ag_2C_2O_4$.
4. A dry oxalate (containing a non-volatile metal) heated in a test-tube evolves carbonic oxide, whilst a carbonate is left which shows effervescence with acids.

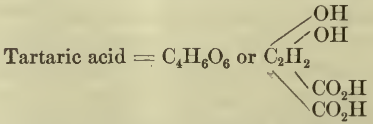
Antidotes to oxalic acid. Calcium carbonate or lime-water should be administered, but no alkalies as in cases of poisoning by mineral acids, because the alkali oxalates are soluble.

Oxalates. The *acid potassium oxalate*, KHC_2O_4, or its combination with oxalic acid, is known under the name of *salt of sorrel.* *Calcium oxalate*, CaC_2O_4, is, in small quantities, a normal constituent of urine. *Ferrous oxalate*, $FeC_2O_4.H_2O$, is made by adding potassium or ammonium oxalate to ferrous sulphate, when double decomposition takes place, and the ferrous oxalate is precipitated as a pale-yellow, crystalline, nearly insoluble powder.

Dibasic acids with alcoholic hydroxyl.



$$\text{Malic acid} = C_4H_6O_5 \text{ or } C_2H_3\left\langle\begin{matrix}OH\\CO_2H\\CO_2H\end{matrix}\right.$$



$$\text{Tartaric acid} = C_4H_6O_6 \text{ or } C_2H_2\left\langle\begin{matrix}OH\\OH\\CO_2H\\CO_2H\end{matrix}\right.$$

In the various acids heretofore considered, the hydrogen is derived either from the unsaturated hydrocarbon residue, or from the hydroxyl in the carboxyl. As shown by the graphic formulas of the above two acids, they contain also hydrogen in the hydroxyl form not in combination with CO. This hydrogen, whilst not replaceable by metals, may be replaced by alcohol radicals; in other words, it behaves like the hydroxyl hydrogen in alcohols. In order to indicate this difference in the function of the hydrogen, malic acid is said to be dibasic, but triatomic; tartaric acid is dibasic and tetratomic. A few other acids behave in a similar manner, as, for instance, lactic acid.

Malic acid, $H_2C_4H_4O_5$, occurs in the juices of many fruits, as apples, currants, etc.

Tartaric acid, Acidum tartaricum, $H_2C_4H_4O_6 = 150$. Frequently found in vegetables, and especially in fruits, sometimes free, generally as the potassium or calcium salt; grapes contain it chiefly as potassium acid tartrate, which is obtained in an impure state as a by-product in the manufacture of wine. During the fermentation of grape-juice, its sugar is converted into alcohol; potassium acid tartrate is less soluble in alcoholic fluids than in water, and therefore is deposited gradually, forming the *crude tartar,* or *argol,* of commerce, a substance containing chiefly potassium acid tartrate, but also calcium tartrate, some coloring matter, and traces of other substances. Crude tartar is the source of tartaric acid and its salts.

Tartaric acid is obtained from potassium acid tartrate by neutralizing with calcium carbonate, and decomposing the remaining neutral potassium tartrate by calcium chloride:

$$\underset{\substack{\text{Potassium acid}\\\text{tartrate.}}}{2(KHC_4H_4O_6)} + \underset{\substack{\text{Calcium}\\\text{carbonate.}}}{CaCO_3} = \underset{\substack{\text{Calcium}\\\text{tartrate.}}}{CaC_4H_4O_6} + \underset{\substack{\text{Potassium}\\\text{tartrate.}}}{K_2C_4H_4O_6} + \underset{\text{Water.}}{H_2O} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2}.$$

$$\underset{\substack{\text{Potassium}\\\text{tartrate.}}}{K_2C_4H_4O_6} + \underset{\substack{\text{Calcium}\\\text{chloride.}}}{CaCl_2} = \underset{\substack{\text{Calcium}\\\text{tartrate.}}}{CaC_4H_4O_6} + \underset{\substack{\text{Potassium}\\\text{chloride.}}}{2KCl}.$$

The whole of the tartaric acid is thus converted into calcium tartrate, which is precipitated as an insoluble powder; this is collected, well washed, and decomposed by boiling with sulphuric acid, when calcium sulphate is formed as an almost insoluble residue, while tartaric acid is left in solution, from which it is obtained by evaporation and crystallization:

$$\underset{\substack{\text{Calcium}\\\text{tartrate.}}}{CaC_4H_4O_6} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Tartaric}\\\text{acid.}}}{H_2C_4H_4O_6} + \underset{\substack{\text{Calcium}\\\text{sulphate.}}}{CaSO_4}.$$

Tartaric acid crystallizes in colorless, transparent prisms; it has a strongly acid, but not disagreeable taste; it is readily soluble in water and alcohol, and fuses at 135° C. (275° F.).

There are three acids which are isomeric with common tartaric acid, differing from it in physical, but not in chemical properties. These acids are known as *inactive tartaric acid*, *levotartaric acid*, and *racemic acid*, whilst the common tartaric acid is termed *dextrotartaric acid.* Crude tartar sometimes contains racemic acid.

Analytical reactions.

(Potassium sodium tartrate, $KNaC_4H_4O_6$, may be used.)

1. Neutral solutions of tartaric acid give with calcium chloride a white precipitate of calcium tartrate, which, after being quickly collected on a filter and washed, is soluble in potassium hydroxide; from this solution calcium tartrate is precipitated on boiling. (Calcium citrate is insoluble in potassium hydroxide.)
2. A strong solution of a tartrate, acidulated with acetic acid, gives a white precipitate of potassium acid tartrate on the addition of potassium acetate. (Precipitate forms slowly.)
3. A neutral solution of a tartrate gives with silver nitrate a white precipitate of silver tartrate, $Ag_2C_4H_4O_6$, which blackens on boiling, in consequence of the decomposition of the salt, with separation of silver. If, before boiling, a drop of ammonia water be added, a mirror of metallic silver will form upon the glass.
4. Sulphuric acid heated with tartrates chars them readily.
5. Tartrates, when heated, are decomposed (blacken), and evolve a somewhat characteristic odor, resembling that of burnt sugar

The above reaction, 3, can be used to advantage for silvering glass by operating as follows: Dissolve 1 gramme of silver nitrate in 20 c.c. of water, add water of ammonia until the precipitate which forms is nearly redissolved, and dilute with water to 100 c.c. Make a second solution by dissolving 0.2 gramme of silver nitrate in 100 c.c. of boiling water, add 0.166 gramme of potassium sodium tartrate, boil until the precipitate becomes gray, and filter. Mix the two solutions cold and set aside for one hour, when a mirror of metallic silver will be found.

Potassium acid tartrate, Potassii bitartras, $KHC_4H_4O_6 = 188$ (*Potassium bitartrate, Cream of tartar*). The formation of this salt in the crude state (argol) has been explained above. It is purified by dissolving in hot water and crystallizing, when it is obtained in colorless crystals, or as a white, somewhat gritty powder of a pleasant, acidulous taste; it is sparingly soluble in cold, easily soluble in hot water.

The name cream of tartar was given to the salt for the reason that small crystals, which float on the liquid, separate on rapidly cooling a hot solution of potassium bitartrate.

Potassium tartrate, $2(K_2C_4H_4O_6).H_2O$. Obtained by saturating a solution of potassium acid tartrate with potassium carbonate:

$$\underset{\text{Potassium acid tartrate.}}{2KHC_4H_4O_6} + \underset{\text{Potassium carbonate.}}{K_2CO_3} = \underset{\text{Potassium tartrate.}}{2K_2C_4H_4O_6} + H_2O + CO_2.$$

Small transparent or white crystals, or a white neutral powder, soluble in less than its own weight of water.

Potassium sodium tartrate, Potassii et sodii tartras, $KNaC_4H_4O_6.4H_2O$ = 282 (*Rochelle salt*). If in the above-described process for making neutral potassium tartrate, sodium carbonate is substituted for potassium carbonate, the double tartrate of potassium and sodium is formed. It is a white powder, or occurs in colorless, transparent crystals which are easily soluble in water.

Experiment 48. Add gradually 24 grammes of potassium acid tartrate to a hot solution of 20 grammes of crystallized sodium carbonate in 100 c.c. of water. Heat until complete solution has taken place, filter, evaporate to about one-half the volume, and set aside for the potassium sodium tartrate to crystallize. How much crystallized sodium carbonate is required for the conversion of 25 grammes of potassium acid tartrate into Rochelle salt?

Seidlitz powders (*Compound effervescing powders*) consist of a mixture of 7.75 grammes (120 grains) of Rochelle salt with 2.58 grammes (40 grains) of sodium bicarbonate (wrapped in blue paper), and 2.25 grammes (35 grains) of tartaric acid (wrapped in white paper). When dissolved in water the tartaric acid acts upon the sodium bicarbonate, causing the formation of sodium tartrate, while the escaping carbon dioxide causes effervescence.

Antimony and potassium tartrate, Antimonii et potassii tartras, $2(KSbO.C_4H_4O_6).H_2O$ = 664 (*Potassium antimonyl tartrate, Tartar emetic*). This salt is made by dissolving freshly prepared antimonous oxide (while yet moist) in a solution of potassium acid tartrate. From the solution somewhat evaporated, tartar emetic separates in colorless, transparent rhombic crystals:

$$\underset{\text{Potassium acid tartrate.}}{2KHC_4H_4O_6} + \underset{\text{Antimonous oxide.}}{Sb_2O_3} = \underset{\text{Tartar emetic.}}{2KSbO.C_4H_4O_6} + H_2O.$$

The fact that not antimony itself, but the group SbO, replaces the hydrogen, has led to the assumption of the hypothetical radical SbO, termed antimonyl.

Tartar emetic is soluble in water, insoluble in alcohol; it has a sweet, afterward disagreeable metallic taste.

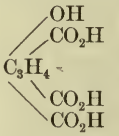
Action of certain organic acids upon certain metallic oxides. The solution of a ferric salt (or certain other metallic salts) is precipitated by alkali hydroxides, a salt of the alkali and ferric hydroxide being formed. When a sufficient quantity of either tartaric, citric, oxalic, or various other organic acids has been added previously to the iron solution (or to certain other metallic solutions) no such precipitate is produced by the alkali hydroxides, because organic salts or double salts are formed which are soluble, and from which the metallic hydroxides are not precipitated by alkali hydroxides. Upon evaporation no crystals (of the organic salt) form, and in order to obtain the compounds in a dry state, the liquid, after being evaporated to the consistence of a syrup, is spread on glass plates which are exposed to a temperature not exceeding 60° C. (140° F.), when brown, green, or yellowish-green, amorphous, shining, transparent scales are formed, which are the *scale compounds* of the U. S. P.

Instead of obtaining these compounds, as stated above, by adding the organic acids (or their salts) to the inorganic salts, they are more generally obtained by dissolving the freshly precipitated metallic hydroxide in the organic acid.

The true chemical constitution of many of these scale compounds has as yet not been determined with certainty.

Of official scale compounds containing tartaric acid may be mentioned the *iron and ammonium tartrate*, and the *iron and potassium tartrate.* The first compound is obtained by dissolving freshly precipitated ferric hydroxide in a solution of ammonium acid tartrate, the second by dissolving ferric hydroxide in potassium acid tartrate. The clear solutions, after having been sufficiently evaporated, are dried, as mentioned above, on glass plates.

Citric acid, Acidum citricum, $H_3C_6H_5O_7.H_2O = 210$. Citric acid is a tribasic acid containing three atoms of hydrogen replaceable by metals; its constitution may be expressed by the graphic formula:



Citric acid is found in the juices of many fruits (strawberry, raspberry, currant, cherry, etc.), and in other parts of plants. It is obtained from the juice of lemons by saturating it with calcium carbonate and decomposing by sulphuric acid the calcium citrate thus formed. (100 parts of lemons yield about 5 parts of the acid.) It forms colorless crystals, easily soluble in water.

Analytical reactions.

(Potassium citrate, $K_3C_6H_5O_7$, may be used.)

1. Neutral solutions of citrates yield with calcium chloride on boiling (not in the cold) a white precipitate of calcium citrate, which is insoluble in potassium hydroxide, but soluble in cupric chloride.

2. Neutral solutions of citrates are precipitated white by silver nitrate. The precipitate does not blacken on boiling, as in the case of tartrates.

3. A neutral or alkaline solution of a citrate to which a few drops of a solution of potassium permanganate have been added, becomes green or reddish-green. Tartrates decolorize permanganate.

Citrates. *Potassium citrate,* $K_3C_6H_5O_7.H_2O$, *Lithium citrate,* $Li_3C_6H_5O_7$, and *Magnesium citrate,* $Mg_3(C_6H_5O_7)_2.14HO_2$, are colorless substances, easily soluble in water and obtained by dissolving the carbonates in citric acid.

The *effervescent citrates of potassium, lithium, and magnesium,* are granulated mixtures of citric acid with potassium bicarbonate, lithium carbonate, and magnesium carbonate respectively; sugar is added to all, and some sodium bicarbonate to the two last preparations.

The official *solution of magnesium citrate* is made by dissolving magnesium carbonate in an excess of citric acid solution to which some syrup is added, and dropping into this mixture, which should be contained in a strong bottle, potassium bicarbonate. The bottle is immediately closed with a cork in order to retain the liberated carbon dioxide.

Bismuth citrate, $BiC_6H_5O_7$, is obtained by boiling a solution of citric acid with bismuth nitrate, when the latter is gradually converted into citrate whilst nitric acid is set free; the insoluble bismuth citrate is collected, washed, and dried; it forms a white, amorphous powder, which is insoluble in water, but soluble in water of ammonia.

Bismuth ammonium citrate is a scale compound obtained by dissolving bismuth citrate in water of ammonia and evaporating the solution at a low temperature.

Ferric citrate, Ferri citras. Obtained in transparent, red scales, by dissolving ferric hydroxide in citric acid and evaporating the solution as mentioned heretofore. By mixing solution of ferric citrate with either water of ammonia, or quinine, strychnine, sodium phosphate, or sodium pyrophosphate, evaporating to the consistence of syrup and drying on glass plates, the following scale compounds are obtained respectively: *Iron and ammonium citrate, iron and quinine* *citrate, iron and strychnine citrate, soluble ferric phosphate,* and *soluble ferric pyrophosphate.*

Lactic acid, Acidum lacticum, $HC_3H_5O_3 = 90$. This acid is the second member of a group of monobasic, diatomic acids which have the general composition $C_nH_{2n}O_3$, and which contain two hydroxyl groups, the hydrogen of one being capable of replacement by metals, the other by alcohols. The first member of this series is *glycolic acid,* $HC_2H_3O_3$, a white, deliquescent, crystalline substance which is found in unripe grapes and in the leaves of the wild grape. Glycolic acid has been shown to be acetic acid, $C_2H_4O_2$, in which one atom of hydrogen has been replaced by hydroxyl. The name hydroxy-acetic acid, has, therefore, been given to this compound.

Lactic acid occurs in many plant-juices; it is formed from sugar by a peculiar fermentation known as "lactic fermentation," which causes the presence of this acid in sour milk and in many sour, fermented substances, as in ensilage, sauer-kraut, etc. The formation of lactic acid from sugar may be expressed by the equation:

$$\underset{\text{Sugar.}}{C_6H_{12}O_6} = \underset{\text{Lactic acid.}}{2(HC_3H_5O_3)}.$$

For practical purposes lactic acid is made by mixing a solution of sugar with milk, putrid cheese, and chalk, and digesting this mixture for several weeks at a temperature of about 30° C. (86° F.). The bacteria in the cheese act as a ferment, and the chalk neutralizes the acid generated during the fermentation. The calcium lactate thus obtained is purified by crystallization and decomposed by oxalic acid, which forms insoluble calcium oxalate.

Lactic acid is a colorless, syrupy liquid, of strongly acid properties; it mixes in all proportions with water and alcohol. The official lactic acid contains 75 per cent. of absolute acid.

A lactic acid called *sarco-lactic acid* is found in meat-juice, and, therefore, as a constituent of meat-extract. This acid has the composition and all the properties of the above ordinary lactic acid, with the exception that it acts differently on polarized light.

Ferrous lactate, Ferri lactas, $Fe(C_3H_5O_3)_2.3H_2O = 287.9$. Made by dissolving iron filings in diluted lactic acid; hydrogen is liberated and the salt formed. It is a pale, greenish-white, crystalline substance, soluble in water.

QUESTIONS.—431. Name the more common organic acids found in vegetables and especially in sour fruits. 432. What is the composition of oxalic acid, how is it manufactured, and what are its properties? 433. Explain the formation of crude tartar during the fermentation of grape-juice, and how is tartaric

Strontium lactate, $Sr(C_3H_5O_3)_2.3H_2O$, is readily obtained by dissolving strontium carbonate in lactic acid. It is a white granular or crystalline powder, readily soluble in water.

45. ETHERS.

Constitution. It has been shown that alcohols are hydrocarbon residues in combination with hydroxyl, OH, and that acids are hydrocarbon residues in combination with carboxyl, CO.OH; it has further been shown that carboxyl may be considered as being composed of CO, and hydroxyl, OH, and that the term acid radical is applied to that group of atoms in acids which embraces the hydrocarbon residue + CO. If we represent an alcohol radical by AlR, and an acid radical by AcR, the general formula of an alcohol is AlR.OH, or $\left.\begin{matrix}AlR\\H\end{matrix}\right\rangle O$, and of an acid, AcR.OH, or $\left.\begin{matrix}AcR\\H\end{matrix}\right\rangle O$.

Ethers are formed by replacement of the hydrogen of the hydroxyl in alcohols by hydrocarbon residues (or alcohol radicals), and *compound ethers* or *esters* are formed by replacement of the hydrogen of the hydroxyl (or carboxyl) in acids by hydrocarbon residues. While alcohols correspond in their constitution to hydroxides, ethers correspond to oxides, and compound ethers to salts. For instance:

Hydroxides.	*Oxides.*	*Acids.*	*Salts.*
$KOH = \left.\begin{matrix}K\\H\end{matrix}\right\rangle O$ Potassium hydroxide.	$K_2O = \left.\begin{matrix}K\\K\end{matrix}\right\rangle O$ Potassium oxide.	$HNO_3 = \left.\begin{matrix}NO_2\\H\end{matrix}\right\rangle O$ Nitric acid.	$KNO_3 = \left.\begin{matrix}NO_2\\K\end{matrix}\right\rangle O$ Potassium nitrate.
$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\rangle O$ Ethyl alcohol.	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle O$ Ethyl ether.	$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\rangle O$ Acetic acid.	$\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\rangle O$ Ethyl acetate, or acetic ether.
$\left.\begin{matrix}AlR\\H\end{matrix}\right\rangle O$ Alcohol.	$\left.\begin{matrix}AlR\\AlR\end{matrix}\right\rangle O$ Ether.	$\left.\begin{matrix}AcR\\H\end{matrix}\right\rangle O$ Acid.	$\left.\begin{matrix}AcR\\AlR\end{matrix}\right\rangle O.$ Compound ether.

It is not necessary that the two hydrocarbon residues in an ether should be alike, as in the above ethyl ether, but they may be different, in which case the ethers are termed *mixed ethers.* For instance:

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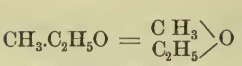
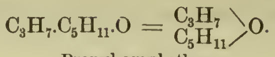
acid obtained from it? 434. Give properties of and tests for tartaric acid. 435. State the composition and formation of cream of tartar, Rochelle salt, and tartar emetic. 436. What are Seidlitz powders, and what changes take place when they are dissolved? 437. Mention some official scale compounds of iron, and give a general outline of the mode of preparing them. 438. From what and by what process is citric acid obtained? 439. Mention tests by which citric acid may be distinguished from tartaric acid. 440. From what and by what process is lactic acid obtained; what are its properties?



$$CH_3.C_2H_5O = \begin{matrix}C\,H_3\\C_2H_5\end{matrix}\Big>O$$

Methyl-ethyl ether.

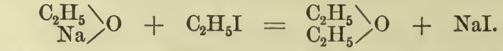


$$C_3H_7.C_5H_{11}.O = \begin{matrix}C_3H_7\\C_5H_{11}\end{matrix}\Big>O.$$

Propyl-amyl ether.

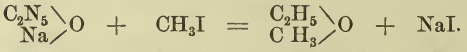
In diatomic or triatomic alcohols, or in dibasic or tribasic acids, containing more than one atom of hydrogen derived from hydroxyl or carboxyl, these hydrogen atoms may be replaced by various other univalent, bivalent, or trivalent residues. This fact shows that the number of ethers or compound ethers which are capable of being formed is very large.

Formation of ethers. Ethers may be formed by the action of the chloride or iodide of a hydrocarbon residue upon an alcohol, in which the hydroxyl hydrogen has been replaced by a metal. For instance:



$$\begin{matrix}C_2H_5\\Na\end{matrix}\Big>O + C_2H_5I = \begin{matrix}C_2H_5\\C_2H_5\end{matrix}\Big>O + NaI.$$

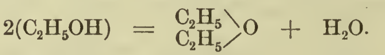
Sodium ethylate. Ethyl iodide. Ethyl ether. Sodium iodide.



$$\begin{matrix}C_2N_5\\Na\end{matrix}\Big>O + CH_3I = \begin{matrix}C_2H_5\\C\,H_3\end{matrix}\Big>O + NaI.$$

Sodium ethylate. Methyl iodide. Ethyl-methyl ether. Sodium iodide.

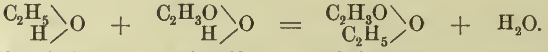
Ethers are also formed by the action of sulphuric acid upon alcohols; the sulphuric acid removing water in this case, thus:



$$2(C_2H_5OH) = \begin{matrix}C_2H_5\\C_2H_5\end{matrix}\Big>O + H_2O.$$

Ethyl alcohol. Ethyl ether. Water.

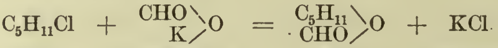
Compound ethers are formed by the combination of acids with alcohols and elimination of water. (Presence of sulphuric acids facilitates this action.)



$$\begin{matrix}C_2H_5\\H\end{matrix}\Big>O + \begin{matrix}C_2H_3O\\H\end{matrix}\Big>O = \begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\Big>O + H_2O.$$

Ethyl alcohol. Acetic acid. Ethyl acetate. Water.

They are also formed by the action of hydrocarbon chlorides (or iodides) on salts. For instance:



$$C_5H_{11}Cl + \begin{matrix}CHO\\K\end{matrix}\Big>O = \begin{matrix}C_5H_{11}\\CHO\end{matrix}\Big>O + KCl.$$

Amyl chloride. Potassium formate. Amyl formate. Potassium chloride.

Occurrence in nature. Many ethers are products of vegetable life and occur in some essential oils; *wax* contains the compound ether melissyl palmitate, $C_{30}H_{61}.C_{16}H_{31}O.O$, and *spermaceti*, a solid substance found in the head of the whale, is cethyl palmitate, $C_{16}H_{33}.C_{16}H_{31}O.O$. The most important group of compound ethers are the fats and fatty oils, which are distributed widely in the vegetable, but even more so in the animal kingdom.

General properties. The ethers and compound ethers of the lower members of the monatomic alcohols and fatty acids have generally a characteristic and pleasant odor. Fruit essences consist mainly of such compound ethers, and what is generally known as the "bouquet" or "flavor" of wine and other alcoholic liquors is due chiefly to ethers or compound ethers, which are formed during (and after) the fermentation by the action of the acids present upon the alcohol or the alcohols formed. The improvement which such alcoholic liquids undergo "by age" is caused by a continued chemical action between the substances named.

All ethers are neutral substances; those formed by the lower alcohols and acids are generally volatile liquids, those of the higher members are non-volatile solids. When compound ethers are heated with alkalies, the acid combines with the latter, whilst the alcohol is liberated. (The properties of the compound ethers, termed fats, will be considered further on.)

Ethyl ether, Æther, $(C_2H_5)_2O = 74$ (*Ether, sulphuric ether, Ethyl oxide*). The name of the whole group of ethers is derived from this (ethyl-) ether, in the same way that common (ethyl-) alcohol has given its name to the group of alcohols. The name sulphuric ether was given at a time when its true composition was yet unknown, and for the reason that sulphuric acid was used in its manufacture.

Ether is manufactured by heating to about 140° C. (284° F.) a mixture of 1 part of alcohol and 1.8 parts of concentrated sulphuric acid in a retort, which is so arranged that additional quantities of alcohol may be allowed to flow into it, while the open end is connected with a tube, leading through a suitable cooler, in order to condense the highly volatile product of the distillation.

Experiment 49. Mix 100 grammes of alcohol with 180 grammes of ordinary sulphuric acid, allow to stand and pour the cooled mixture into a flask which is provided with a perforated cork through which pass a thermometer and a bent glass tube leading to a Liebig's condenser. Apply heat and notice that the liquid commences to boil at about 140° C. (284° F.). Distil about 50 c.c., pour this liquid into a stoppered bottle and add an equal volume of water. Ethyl ether will separate into a distinct layer over the water, and may be removed by means of a pipette. Repeat the washing with water, add to the ether thus freed from alcohol a little calcium chloride and distil it from a dry flask, standing in a water-bath. The greatest care should be exercised and the neighborhood of flames avoided in working with ether, on account of its volatility and the inflammability of its vapors.

The apparatus described above for etherification can be constructed so as to make the process continuous. This may be done by using with the boiling-flask a cork with a third aperture through which a glass tube passes into the liquid. The other end of the tube is connected by means of rubber tubing with a vessel filled with alcohol and standing somewhat above the flask. As soon as distillation commences alcohol is allowed to flow into the flask at a rate equal to that of the distillation, keeping the temperature at about 140° C. (284° F.). The flow of alcohol is regulated by a stop-cock.

The action of sulphuric acid upon alcohol is not quite so simple as described above in connection with the general methods for obtaining ethers, where the final result only was given An intermediate product, known as *ethyl-sulphuric acid* or *sulpho-vinic acid*, is formed, which, by acting upon another molecule of alcohol, forms sulphuric acid and ether, which latter is volatilized as soon as formed. The decomposition is shown by the equations:

$$\underset{\text{Alcohol.}}{C_2H_5OH} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Ethyl-sulphuric}\\\text{acid.}}}{C_2H_5HSO_4} + \underset{\text{Water.}}{H_2O}.$$

$$\underset{\substack{\text{Ethyl-sulphuric}\\\text{acid.}}}{C_2H_5HSO_4} + \underset{\text{Alcohol.}}{C_2H_5OH} = \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} + \underset{\text{Ether.}}{(C_2H_5)_2O}.$$

The liberated sulphuric acid at once attacks another molecule of alcohol, again forming ethyl-sulphuric acid, which is again decomposed, etc. Theoretically, a given quantity of sulphuric acid should be capable, therefore, of converting any quantity of alcohol into ether; practically, however, this is not the case, because secondary reactions take place simultaneously, and because the water which is constantly formed does not all distil with the ether, and therefore dilutes the acid to such an extent that it no longer acts upon the alcohol.

Ether thus obtained is not pure, but contains water, alcohol, sulphurous and sulphuric acids, etc.; it is purified by mixing it with chloride and oxide of calcium, pouring off the clear liquid and distilling it.

The official ether contains of ethyl-ether 96 per cent. and of alcohol 4 per cent. It is a very mobile, colorless, highly volatile liquid, of a refreshing, characteristic odor, a burning and sweetish taste, and a neutral reaction; it is soluble in alcohol, chloroform, liquid hydrocarbons, fixed and volatile oils, and dissolves in ten volumes of water. Specific gravity is 0.726 at 15° C. (59° F.); boiling-point 37° C. (98.6° F.). It is easily combustible and burns with a luminous flame. When inhaled, it causes intoxication and then loss of consciousness and sensation. The great volatility and combustibility of ether necessitate special care in the handling of this substance near fire or light.

Spiritus ætheris and *Spiritus ætheris compositus* are mixtures of about one part of ether and two parts of alcohol, 3 per cent. of certain ethereal oils being added to the second preparation.

Acetic ether, Æther aceticus, $C_2H_5C_2H_3O_2 = 88$ (*Ethyl acetate*). Made by mixing dried sodium acetate with alcohol and sulphuric acid, distilling and purifying the crude product by shaking with calcium chloride and rectifying :

$$\underset{\text{Ethyl alcohol.}}{C_2H_5OH} + \underset{\text{Sodium acetate.}}{NaC_2H_3O_2} + H_2SO_4 = \underset{\text{Acetic ether.}}{C_2H_5C_2H_3O_2} + \underset{\text{Sodium acid sulphate.}}{NaHSO_4} + H_2O.$$

Experiment 50. Add to a mixture of 40 grammes of pure alcohol and 100 grammes of concentrated sulphuric acid 60 grammes of sodium acetate. Introduce this mixture into a boiling-flask, connect it with a Liebig's condenser and distil about 50 c.c. Redistil the liquid from a flask, as represented in Fig. 39, page 298, and collect the portion which passes over at a temperature of 77° C. (170° F.); it is nearly pure ethyl acetate.

Acetic ether is a colorless, neutral, and mobile liquid, of a strong ethereal and somewhat acetous odor, soluble in alcohol, ether, chloroform, etc., in all proportions, and in 17 parts of water. Specific gravity 0.894. Boiling-point 76° C. (169° F.)

Ethyl nitrite, $C_2H_5NO_2$ (*Nitrous ether*). Made by distilling a mixture of alcohol, sulphuric acid, and sodium nitrite :

$$C_2H_5OH + NaNO_2 + H_2SO_4 = C_2H_5NO_2 + NaHSO_4 + H_2O$$

The distillate, which contains, besides ethyl nitrite, some alcohol and often some decomposition products, is washed with ice-cold water, in which ethyl nitrite is nearly insoluble, and with sodium carbonate to remove traces of acid ; finally, it is freed from water by treatment with anhydrous potassium carbonate.

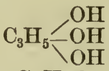
Spirit of nitrous ether, Spiritus ætheris nitrosi, Sweet spirit of nitre. This is a mixture of about 4 parts of ethyl nitrite with 96 parts of alcohol. It is a clear, mobile, volatile, and inflammable liquid, of a pale straw color inclining slightly to green, a fragrant, ethereal odor, and a sharp, burning taste. It is neutral, or but very slightly acid to litmus paper but evolves no carbon dioxide with potassium bicarbonate.

Amyl nitrite, Amyl nitris, $C_5H_{11}NO_2 = 117$. Made by a process analogous to the one mentioned above for ethyl nitrite, substituting amyl alcohol for ethyl alcohol.

The official amyl nitrite contains of this ether about 80 per cent., together with variable quantities of undetermined compounds; it is a clear, pale-yellowish liquid, of an ethereal, fruity odor, an aromatic taste, and a neutral or slightly acid reaction. Specific gravity 0.872. Boiling-point 96° C. (205° F.).

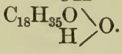
Fats and fat oils. All true fats are compound ethers of the triatomic alcohol glycerin, in which the three replaceable hydrogen atoms of the hydroxyl are replaced by three univalent radicals of the higher members of the fatty acids. For instance:

Glycerin = $C_3H_5.(OH)_3$ or



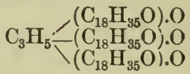
$$C_3H_5\begin{cases}OH\\OH\\OH\end{cases}$$

Stearic acid = $C_{18}H_{35}O.OH$ or



$$\left.\begin{matrix}C_{18}H_{35}O\\H\end{matrix}\right\rangle O.$$

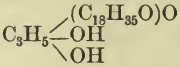
Stearin or tristearin = $C_3H_5.(C_{18}H_{35}O)_3.O_3$ or



$$C_3H_5\begin{cases}(C_{18}H_{35}O).O\\(C_{18}H_{35}O).O\\(C_{18}H_{35}O).O\end{cases}$$

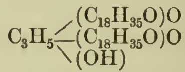
While all natural fats are glycerin in which the three hydrogen atoms are replaced, we may by artificial means introduce but one or two acid radicals, thus forming:

Monostearin =



$$C_3H_5\begin{cases}(C_{18}H_{35}O)O\\OH\\OH\end{cases}$$

Distearin =



$$C_3H_5\begin{cases}(C_{18}H_{35}O)O\\(C_{18}H_{35}O)O\\(OH)\end{cases}$$

Fats are often termed *glycerides;* stearin being, for instance, the glyceride of stearic acid.

The principal fats consist of mixtures of palmitin, $C_3H_5.(C_{16}H_{31}O)_3.O_3$, stearin, $C_3H_5.(C_{18}H_{35}O)_3.O_3$, and olein, $C_3H_5.(C_{18}H_{33}O)_3.O_3$. Stearin and palmitin are solids, olein is a liquid at ordinary temperature; the relative quantity of the three fats mentioned determines its solid or liquid condition. The liquid fats, containing generally olein as their chief constituent, are called *fatty oils* or *fixed oils* in contradistinction to volatile or essential oils.

All fats, when in a pure state, are colorless, odorless, and tasteless substances, which stain paper permanently; they are insoluble in water, difficultly soluble in cold alcohol, easily soluble in ether, disulphide of carbon, benzene, etc. The taste and color of fats are due to foreign substances, often produced by a slight decomposition which has taken place in some of the fat. All fats are lighter than water, and all solid fats fuse below 100° C. (212° F.); fats can be distilled without change at about 300° C. (572° F.), but are decomposed at a higher temperature with the formation of numerous products, some of which have an extremely disagreeable odor, as, for instance, *acrolein*, C_3H_4O, an aldehyde which in composition is equal to glycerin minus two molecules of water:

$$C_3H_5(HO)_3 \quad - \quad 2H_2O \quad = \quad C_3H_4O.$$

Some fats keep without change when pure; since they contain, however, impurities generally, such as albuminous matter, etc., they suffer decomposition (a kind of fermentation aided by oxidation), which results in a liberation of the fatty acids, which impart their odor and taste to the fats, causing them to become what is generally termed *rancid.*

Some fats, especially some oils, suffer oxidation, which renders them hard. These *drying oils* differ from other oils in being mixtures of olein with another class of glycerides, containing unsaturated acids with less hydrogen in relation to carbon than oleic acid. Drying oils are prevented from drying by albuminous impurities, which may be removed by treating the oil with 4 per cent of concentrated sulphuric acid; the acid does not act on the fat, but quickly destroys the albuminous matters, which, with the sulphuric acid, sink to the bottom, whilst the "refined" oil may be removed by decantation.

Fats are largely distributed in the animal and vegetable kingdoms. They exist in plants chiefly in the seeds, while in animals they are found generally under the skin, around the intestines, and on the muscles.

Human fat, beef tallow, mutton tallow, and *lard* are mixtures of palmitin and stearin with some olein. *Butter* consists of the glycerides of butyric acid, caproïc acid, caprylic acid, and capric acid, which are volatile with water vapors, and of myristic, palmitic, and stearic acids, which are not volatile.

The principal non-drying vegetable oils (consisting chiefly of olein) are *olive oil, cottonseed oil, cocoanut oil, palm oil, almond oil.*

Among the drying oils are of importance: *linseed oil, castor oil, croton oil, hemp oil, cod-liver oil.*

Whenever fats are treated with alkaline hydroxides, or with a number of other metallic oxides, decomposition takes place, the fatty acids combining with the metals, whilst glycerin is set free. Some of the substances thus formed are of great importance, as, for instance, the various kinds of soap.

Soap. Any fat boiled with sodium or potassium hydroxide will form soap. Soft soap is potassium soap, hard soap is sodium soap. The better kinds of hard soap are made by boiling olive oil with sodium hydroxide:

$$\underset{\text{(olive oil).}}{\underset{\text{Oleate of glyceryl}}{C_3H_5(C_{18}H_{33}O_2)_3}} + \underset{\text{hydroxide.}}{\underset{\text{Sodium}}{3NaOH}} = \underset{\text{(hard soap).}}{\underset{\text{Sodium oleate}}{3NaC_{18}H_{33}O_2}} + \underset{\text{Glycerin.}}{C_3H_5(OH)_3.}$$

Experiment 51. Boil 50 grammes of olive oil with 60 c.c. of a 15 per cent. sodium hydroxide solution for about one hour. The soap which is thereby formed remains dissolved in or mixed with water and glycerin. Cause separation by adding a solution of 15 grammes of sodium chloride in 40 c.c. of water and boiling for a short while, when the soap, which is insoluble in the salt solution, rises to the surface and solidifies on cooling.

Soaps are soluble in water and alcohol; they contain rarely less than 30 per cent., but sometimes as much as 70–80 per cent. of water.

Ammonia liniment, Linimentum ammoniæ, and *lime liniment, Linimentum calcis,* are obtained by mixing cottonseed oil with water of ammonia and lime-water, respectively. The oleate of ammonium or calcium is formed, and remains mixed with the liberated glycerin.

Lead plaster, Emplastrum plumbi. Chiefly lead oleate, $Pb(C_{18}H_{33}O_2)_2$. Obtained by boiling lead oxide with olive oil and water for several hours, until a homogeneous, pliable, and tenacious mass is formed. Lead oleate differs from the oleates of the alkalies by its complete insolubility in water.

Wool-fat, Lanolin. This is the fat, or a mixture of fats, found in sheep's wool and obtained by treating the wool with soap-water, and acidifying the wash liquor, when the fats separate unchanged. These fats differ from the fats spoken of above in so far as the alcohol present is not glycerin, but an alcohol, or rather two isomeric alcohols of the composition $C_{26}H_{43}OH$ and known as *cholesterin* and *iso-cholesterin.* These alcohols, which are white, crystalline, fusible substances, when in combination with fatty acids form the compound ethers known as lanolin.

Lanolin is a yellowish-white (or, when not sufficiently purified, a more or less brownish), fat-like substance, having the peculiar odor of sheep's wool and fusing at about 40° C. (104° F.), forming an oily liquid. Unlike true fats, lanolin is capable of mixing with twice its weight of water or aqueous solutions and yet retaining its fatty consistency; it is, moreover, much less liable to decompose than fats, and it is this property and its power to mix with aqueous solutions which have rendered lanolin a valuable agent in certain pharmaceutical preparations. Official is *hydrous wool-fat,* the purified fat mixed with not more than 30 per cent. of water.

QUESTIONS —441. Explain the constitution of simple, mixed, and compound ethers. To what inorganic compounds are they analogous? 442. State the general processes for the formation of ethers and compound ethers. 443. What is the composition of ethyl ether? Explain the process of its manufacture in words and symbols, and state its properties. 444. How is acetic ether made, and what are its properties? 445. What is sweet spirit of nitre, and how is it made? 446. State the general composition of fats and the chief constituents of tallow, butter, and olive oil. 447. What is the solubility of fats in water, alcohol, and ether; how do heat and oxygen act upon them; what is the cause of their becoming rancid? 448. Explain the composition and manufacture of soap, and state the difference between hard and soft soap. 449. How are ammonia liniment, lime liniment, and lead plaster made, and what is their composition? 450. What is the source of lanolin; what are its constituents and properties?

46. CARBOHYDRATES.

Constitution. The term carbohydrates or carbhydrates is not well chosen, because it implies that these substances are carbon in combination with water. Carbohydrates do contain hydrogen and oxygen in the proportion of two atoms of hydrogen to one atom of oxygen, or in the proportion to form water, but this does not exist as such in the carbohydrates.

The true atomic structure of carbohydrates is as yet but little known. The compounds of the composition $C_6H_{12}O_6$ are now looked upon as the aldehyde of the hexatomic alcohol mannite, $C_6H_{14}O_6$, the chief constituent of manna:

$$C_6H_{14}O_6 \ - \ 2H \ = \ C_6H_{12}O_6.$$

Mannite itself is formed from the saturated hydrocarbon C_6H_{14}, by replacement of 6 atoms of hydrogen by 6OH; its constitutional formula is, therefore, $(C_6H_8)^{vi}.(OH)_6$.

Carbohydrates generally contain 6 atoms of carbon or a multiple of 6.

Properties. Carbohydrates are either fermentable, or can, in most cases, be converted into substances which are capable of fermentation. They are not volatile, but suffer decomposition when sufficiently heated; they have neither acid nor basic properties, but are of a neutral reaction. Oxidizing agents convert them into saccharic and mucic acids and finally into oxalic acid. (Soluble carbohydrates have the property of bending the plane of polarized light.)

Most carbohydrates are white, solid substances, and, with the exception of a few, soluble in water. The members of the first two groups (glucoses and saccharoses) have a more or less sweet taste. Many of them, especially glucoses, are good reducing agents, as is shown by the fact that they deoxidize in alkaline solution salts (or oxides) of copper, bismuth, mercury, gold, etc., either to a lower state of oxidation or to the metallic state.

Occurrence in nature. No other organic substances are found in such immense quantities in the vegetable kingdom as the members of this group, cellulose being a chief constituent of all, starch and various kinds of sugar of most plants. Carbohydrates are also found as products of animal life, as, for instance, the sugar in milk, in bees' honey, etc.

Groups of carbohydrates.

		Glucoses.	*Saccharoses.*	*Amyloses.*
		$C_6H_{12}O_6$.	$C_{12}H_{22}O_{11}$.	$C_6H_{10}O_5$.
Origin	Vegetable	Grape-sugar,	Cane-sugar,	Starch,
		Fruit-sugar,	Melitose,	Dextrin,
		Mannitose,	Maltose,	Gums,
		....	....	Cellulose,
	Animal	Inosite.	Milk-sugar.	Glycogen.

Grape-sugar, $C_6H_{12}O_6$ (*Ordinary glucose, Dextrose*). This substance is very abundantly diffused throughout the vegetable kingdom, and is generally accompanied by fruit-sugar. It is contained in large quantities in the juice of many fruits; the percentage of grape-sugar in the dried fig is about 65, in grape 10–20, in cherry 11, in mulberry 9, in strawberry 6, etc.

Grape-sugar is found also in honey and in minute quantities in the normal blood (0.1 per cent. or less), and traces occur, perhaps, in normal urine, the quantity in both liquids rising, however, during certain diseases, as high as 5 per cent. or higher.

Grape-sugar is produced in the plant from starch by the action of the vegetable acids present; it may be obtained artificially from starch (and from many other carbohydrates) by heating with dilute mineral (sulphuric) acids, which convert starch first into dextrin and then into grape-sugar. Corn-starch is now largely used for that purpose, the excess of sulphuric acid being removed by treating the solution with chalk; the filtered solution is either evaporated to a syrup and sold as "glucose," or evaporated to dryness, when the commercial "grape-sugar" is obtained.

Experiment 52. Heat to boiling 100 c.c. of a 1 per cent. sulphuric acid and add to it very gradually and under constant stirring a mixture made by rubbing together 25 grammes of starch and 25 grammes of water. Continue to boil until iodine no longer causes a blue color (which shows complete conversion of starch into either dextrin or glucose), and until 1 c.c. of the solution is no longer precipitated on the addition of 6 c.c. of alcohol (which shows the conversion of dextrin into sugar, dextrin being precipitated by alcohol). Apply to a portion of the glucose solution thus obtained, and neutralized by sodium carbonate, the tests mentioned below. To the remaining solution add a quantity of precipitated calcium carbonate sufficient to convert all sulphuric acid into calcium sulphate. Filter, evaporate the solution to a syrup and notice its sweet taste.

Glucose is met with generally as a thick syrup which crystallizes with difficulty, combining during crystallization with one molecule of water; but anhydrous crystals, closely resembling those of cane-sugar, are also known. Glucose is soluble in its own weight of water and is less sweet than cane-sugar, the sweetness of glucose compared to that of cane-sugar being about 3 to 5; when heated to 170° C. (338° F.) it loses water, and is converted into *glucosan*, $C_6H_{10}O_5$; by stronger heating it loses more water and forms *caramel*, a mixture of various substances; it turns the plane of polarized light to the right.

Grape-sugar combines with various metallic oxides (alkalies, alkaline earths, etc.), and also with a number of other substances, forming a series of compounds known as glucosides.

Grape-sugar may be recognized analytically:

1. By causing a bright-red precipitate of cuprous oxide, when boiled with a solution of cupric sulphate in sodium hydroxide, to which tartaric acid has been added. (A solution containing these three substances in definite proportions is known as Fehling's solution. See index.)

2. By precipitating metallic silver, bismuth, and mercury, when compounds of these metals are heated with it in the presence of caustic alkalies.

3. By easily fermenting when yeast is added to the solution, alcohol and carbon dioxide being formed:

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2.$$

Fruit-sugar, $C_6H_{12}O_6$ (*Levulose*), occurs with glucose in sweet fruits and honey; it resembles glucose in most chemical and physical properties, but does not crystallize from an aqueous solution; it may, however, be obtained in white, silky needles from an alcoholic solution; it is met with generally as a thick syrup, is about as sweet as cane-sugar, and turns the plane of polarized light to the left; it is formed by the action of dilute mineral acids or ferments on cane-sugar, which latter takes up water and breaks up thus:

$$\underset{\text{Cane-sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Levulose.}}{C_6H_{12}O_6}.$$

Mannitose, $C_6H_{12}O_6$. Obtained by the oxidation of mannite; it does not crystallize and resembles grape-sugar.

Galactose, $C_6H_{12}O_6$, is formed together with dextrose when either milk-sugar or gum-arabic is boiled with dilute sulphuric acid. Galactose crystallizes, reduces an alkaline copper solution, but does not ferment with yeast.

Inosite, $C_6H_{12}O_6$ (*Muscle-sugar*), occurs in various muscular tissues, in the lungs, kidneys, liver, spleen, brain, and blood. Although identical in composition with grape-sugar, inosite differs from the latter in not being fermentable and by not precipitating cuprous oxide from alkaline copper-solutions.

Cane-sugar, Saccharum, $C_{12}H_{22}O_{11} = 342$ (*Ordinary saccharose, Common sugar, Beet-sugar*). Cane-sugar is found in the juices of many plants, especially in that of the different grasses (sugar-cane), and also in the sap of several forest trees (maple), in the roots, stems, and other parts of various plants (sugar-beet), etc. Plants containing cane-sugar do not contain free organic acids, which latter would convert it into grape-sugar.

Cane-sugar is manufactured from various plants containing it by crushing them between rollers, expressing the juice, heating and adding to it milk of lime, which precipitates vegetable albuminous matter. The clear liquid is evaporated to the consistency of a syrup, which is further purified (refined) by filtering it through bone-black and evaporating the solution in "vacuum pans" to the crystallizing-point; the mother-liquors are further evaporated, and yield lower grades of sugar; finally a syrup is left which is known as *molasses.*

Cane-sugar forms white, hard, distinctly crystalline granules, but may be obtained also in well-formed, large, monoclinic prisms. It dissolves in 0.2 part of boiling, in 0.5 part of cold water, and in 175 parts of alcohol; when heated to 160° C. (320° F.) it fuses, and the liquid, on cooling, forms an amorphous, transparent mass, known as *barley sugar;* at a higher temperature cane sugar is decomposed, water is evolved, and a brown, almost tasteless substance is formed, which is known as *caramel* or burnt sugar. Oxidizing agents act energetically upon cane-sugar, which is a strong reducing agent. A mixture of cane-sugar and potassium chlorate will deflagrate when moistened with sulphuric acid; potassium permanganate is readily deoxidized in acid solution; cane-sugar, however, does not affect an alkaline copper-solution, and does not ferment itself; but when heated with dilute acids or left in contact with yeast for some time, it is decomposed into dextrose and levulose, both of which are fermentable. Like dextrose, cane-sugar forms compounds with metals, metallic oxides, and salts, which compounds are known as *sucrates.*

Experiment 53. Make a one per cent. cane-sugar solution; test it with Fehling's solution and notice that no cuprous oxide is precipitated. Add to 50 c c. of the cane-sugar solution 5 drops of hydrochloric acid and heat on a water-bath for half an hour. Again examine the liquid with Fehling's solution; a precipitate of cuprous oxide is now formed, proving the conversion of cane-sugar into glucose.

Maltose, $C_{12}H_{22}O_{11}$, is obtained by the action of *diastase* on starch. Diastase is a substance formed during the germination of various seeds (rye, wheat, barley, etc.), and it is for this reason that grain used for alcoholic liquors is allowed to germinate, during which process diastase is formed, which, acting upon the starch present, converts it into maltose and dextrin:

$$\underset{\text{Starch.}}{3(C_6H_{10}O_5)} + H_2O = \underset{\text{Maltose.}}{C_{12}H_{22}O_{11}} + \underset{\text{Dextrin.}}{C_6H_{10}O_5}.$$

Maltose is also formed by the action of dilute sulphuric acid upon starch, and is hence often present in commercial glucose; by further treatment with sulphuric acid it is converted into dextrose. Maltose crystallizes, reduces alkaline copper solutions, and ferments with yeast.

Melitose, $C_{12}H_{22}O_{11}$, is the chief constituent of Australian manna.

Milk-sugar, Saccharum lactis, $C_{12}H_{22}O_{11} + H_2O = 360$ (*Lactose*). Found almost exclusively in the milk of the mammalia. Obtained by freeing milk from casein and fat and evaporating the remaining liquid (whey) to a small bulk, when the milk-sugar crystallizes on cooling.

It forms white, hard, crystalline masses; it is soluble in about 6 parts of water (at 15° C., 59° F.) and in 1 part of boiling water, insoluble in alcohol and ether; it is much harder than cane-sugar, and but faintly sweet; it is not easily brought into alcoholic fermentation by the action of yeast, but easily undergoes "lactic fermentation" when cheese is added. During this process milk-sugar is converted into lactic acid.

Milk-sugar resembles grape-sugar in its action on alkaline solution of copper, from which it precipitates cuprous oxide.

Starch, Amylum, $C_6H_{10}O_5 = 162$. Starch is very widely distributed in the vegetable kingdom, and is found chiefly in the seeds of cereals and leguminosæ, but also in the roots, stems, and seeds of nearly all plants.

It is prepared from wheat, potatoes, rice, beans, sago, arrow-root, etc., by a mechanical operation. The vegetable matter containing the starch is comminuted by rasping or grinding, in order to open the cells in which it is deposited, and then steeped in water; the softened mass is then rubbed on a sieve under a current of water which washes out the starch, while cellular fibrous matter remains on the sieve; the starch deposits slowly from the washings, and is further purified by treating it with water.

Starch forms white, amorphous, tasteless masses, which are peculiarly slippery to the touch, and easily converted into a powder; it is insoluble in cold water, alcohol, and ether; when boiled with water, it yields a white jelly (mucilage of starch, starch-paste) which cannot be looked upon as a true solution, but is a suspension of the swollen starch particles in water; by continued boiling with much water some starch passes into solution.

Starch, when examined under the microscope, is seen to consist of granules differing in size, shape, and appearance, according to the plant from which the starch was obtained. Concentric layers, which are more or less characteristic of starch-granules, show that they are formed in the plant by a gradual deposition of starch matter.

The most characteristic test for starch is the dark-blue color which iodine imparts to it (or better to the mucilage). This color is due to the formation of *iodized starch*, an unstable dark-blue compound of the doubtful composition $C_6H_9IO_5I$.

Starch is an important article of food, especially when associated, as in ordinary flour, with albuminous substances.

Dextrin, $C_6H_{10}O_5$ (*British gum*). Obtained by boiling starch with diluted acids, or by subjecting starch to a dry heat of 175° C. (347° F.) or by the action of diastase (infusion of malt) upon hydrated starch. Malt is made by steeping barley in water until it germinates, and then drying it.

Dextrin is a colorless or slightly yellowish, amorphous powder, resembling gum-arabic in some respects; it is soluble in water, reduces alkaline copper solutions, and is colored light wine-red by iodine. It is extensively used in mucilage as a substitute for gum-arabic.

Gums. These are amorphous substances of vegetable origin, soluble in water or swelling up in it, forming thick, sticky masses; they are insoluble in alcohol, and are converted into glucose by boiling with dilute sulphuric acid. Some gums belong to the saccharoses, others to the amyloses.

Acacia, Gum-arabic is a gummy exudation from Acacia Senegal; it consists chiefly of the calcium salt of *arabic acid*, $C_{12}H_{22}O_{11}$. Other gums occur in the cherry tree, in linseed or flaxseed, in Irish moss, in marsh-mallow root, etc.

Gum-arabic dissolves slowly in 2 parts of water; this solution shows an acid reaction with litmus, and yields precipitates with lead acetate or ferric chloride.

Cellulose, $C_6H_{10}O_5$, perhaps $C_{18}H_{30}O_{15}$ (*Plant fibre, Lignine*). Cellulose constitutes the fundamental material of which the cellular membrane of vegetables is built up, and forms, therefore, the largest portion of the solid parts of every plant; it is well adapted to this purpose on account of its insolubility in water and most other solvents, its resistance to either alkaline or acid liquids, and its tough and flexible nature. Some parts of vegetables (cotton, hemp, and flax, for instance) are nearly pure cellulose.

Pure cellulose is a white, translucent mass, insoluble in all the common solvents, but soluble in an ammoniacal solution of basic cupric carbonate; it is not colored blue by iodine.

Treated with concentrated sulphuric acid it swells up, and gradually dissolves; water precipitates from such solutions a substance known as *amyloid*, which is an altered cellulose giving a blue color with iodine. Upon diluting the sulphuric acid solution with water and boiling it, the cellulose is gradually converted into dextrin and dextrose.

Unsized paper (which is chiefly cellulose) dipped into a mixture of two volumes of sulphuric acid and one volume of water, forms, after being washed and dried, the so-called "parchment paper," which possesses all the valuable properties of parchment.

Pyroxylin, Pyroxylinum, $C_6H_8O_3(NO_3)_2$ (*Cellulose dinitrate, Soluble gun-cotton, Nitro-cellulose*). By the action of nitric acid of various strengths on cellulose, three different substitution products (possibly compound ethers) may be obtained, which are distinguished as cellulose mono-, di-, and trinitrate:

$$\begin{aligned} C_6H_{10}O_5 &+ HNO_3 = H_2O + C_6H_9O_4NO_3. \\ C_6H_{10}O_5 &+ 2HNO_3 = 2H_2O + C_6H_8O_3(NO_3)_2 \\ C_6H_{10}O_5 &+ 3HNO_3 = 3H_2O + C_6H_7O_2(NO_3)_3. \end{aligned}$$

Cellulose trinitrate is the highly explosive *gun-cotton;* an intimate mixture of gun-cotton and camphor is now extensively used under the name of *celluloid.* Cellulose dinitrate or pyroxylin is soluble in a mixture of ether and alcohol; this solution is known as *collodion.*

Experiment 54. Immerse 2 grammes of dry cotton for ten hours in a previously cooled mixture of 28 c.c. of nitric acid and 44 c.c. of sulphuric acid. Wash the pyroxylin thus obtained with cold water until the washings have no longer an acid reaction. Dissolve 1 gramme of the dry pyroxylin in a mixture of 25 c.c. of ether and 8 c.c. of alcohol. The solution obtained is collodion.

Glycogen, $C_6H_{10}O_5$. Found exclusively in animals; it occurs in the liver, the white blood-corpuscles, in many embryonic tissues, and in muscular tissue. Pure glycogen is a white, starch-like, amorphous substance, soluble in water, insoluble in alcohol; by the action of dilute acids it is converted into glucose.

Glucosides. This term is applied to a group of substances (chiefly of vegetable origin) which, by the action of acids, alkalies, or ferments, suffer decomposition in such a manner that one of the products formed is grape-sugar. Glucosides may, therefore, be looked upon as compound sugars, or sugar in combination with various other substances. The following is a list of the more important glucosides, giving also their composition and the sources whence they are obtained:

Amygdalin,	$C_{20}H_{27}NO_{11}$	Bitter almonds, etc.
Cathartic acid,	$C_{180}H_{192}N_4SO_{82}$?	Senna.
Carminic acid,	$C_{17}H_{18}O_{10}$	Cochineal.
Colocynthin,	$C_{58}H_{84}O_{23}$?	Colocynthis.
Digitalin,	?	Digitalis
Gentiopicrin,	$C_{30}H_{30}O_{12}$	Root of gentiana.
Glycyrrhizin,	$C_{24}H_{36}O_9$	Liquorice root.
Helleborin,	$C_{36}H_{42}O_6$	Root of hellebore.
Indican,	$C_{26}H_{31}NO_{17}$	Indigo plant.
Myronic acid,	$C_{10}H_{19}NS_2O_{10}$	Seeds of black mustard.
Salicin,	$C_{13}H_{18}O_7$	Bark of willow.
Tannins,	$C_{14}H_{10}O_9$	In many barks, leaves, etc.

Digitalin. The leaves of digitalis purpurea contain a number of glucosides, mixtures of which in varying proportions form the official article sold under above name. *Digitonin* is an amorphous, yellowish substance, soluble in alcohol. *Digitaleïn* is a white, intensely bitter, amorphous substance. *Digitoxin* is a colorless, crystalline solid; it is the most poisonous of the constituents of digitalin, and is found in the leaves only to the extent of 0.01 to 0.02 per cent.; it is not a glucoside. *Digitalin,* $(C_5H_8O_2)x$, is a white amorphous powder, soluble at ordinary temperature in about 1000 parts of water and in about 100 parts of alcohol of 50 per cent. It is soluble in concentrated hydrochloric acid, forming a golden yellow solution. A similar yellow solution is obtained by dissolving it in concentrated sulphuric acid, the color gradually changing to blood-red. The yellow color of the sulphuric acid solution changes to a beautiful violet on the addition of a drop of nitric acid or ferric chloride.

Myronic acid, $C_{10}H_{19}NS_2O_{10}$, is found as the potassium salt, which is known as *sinigrin,* in black mustard seed. When treated with solution of *myrosin,* a substance also contained in mustard seed and acting as a ferment upon myronic acid or its salts, potassium myronate is converted into dextrose, allyl mustard oil, and potassium bisulphate:

$$\underset{\text{Potassium myronate.}}{KC_{10}H_{18}NS_2O_{10}} = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Allyl mustard oil.}}{C_3H_5NCS} + \underset{\text{Potassium bisulphate.}}{KHSO_4}.$$

The univalent radical allyl, $C_3H_5{}^{i}$, is isomeric, but not identical with the trivalent radical glyceryl, $C_3H_5{}^{iii}$. The triatomic alcohol glycerin, $C_3H_5(OH)_3$, may, however, be converted into the monatomic allyl alcohol C_3H_5OH, by various processes. From allyl alcohol an artificial allyl mustard oil is manufactured.

Allyl sulphide, $(C_3H_5)_2S$, is the chief constituent of the oil of garlic.

Elaterin, $C_{20}H_{28}O_5$. Obtained from the fruit of Ecballium elaterium. It is not a glucoside and its constitution is unknown; it forms white crystals which have a slightly acrid, bitter taste, are almost insoluble in water, have a neutral reaction, and impart to cold concentrated sulphuric acid at first a yellow color, which gradually changes to scarlet.

Picrotoxin $C_{30}H_{34}O_{13}$. Obtained from the seed of Anamirta paniculata. Like elaterin, this is not a glucoside and its constitution is unknown. The white crystals have a very bitter taste, are somewhat soluble in water, have a neutral reaction, and impart to cold concentrated sulphuric acid a golden-yellow color, very gradually changing to reddish-brown, and showing a brown fluorescence.

47. AMINES AND AMIDES. CYANOGEN COMPOUNDS.

Forms of nitrogen in organic compounds. Nitrogen may be present in organic compounds in three forms, viz., ammonia, cyanogen, nitric acid, or derivatives of these compounds. Substances containing nitrogen in the nitric acid form may be obtained by combination of nitric acid with organic basic substances, when salts are formed, or with alcohols, when compound ethers result. In some cases the nitric acid radical NO_2 may replace one or more hydrogen atoms in

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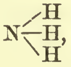
QUESTIONS.—451. To which group of substances is the term "carbohydrates" applied? 452. State the general properties of carbohydrates. 453. Mention the three groups of carbohydrates, and the composition and characteristics of the members of each group. 454. Mention some fruits in which grape-sugar, and some plants in which cane-sugar is found. 455. What is the difference between grape-sugar and cane-sugar, and by what tests can they be distinguished? 456. From what source, and by what process, is milk-sugar obtained? 457. What is starch, what are its properties, by what tests can it be recognized, and what substance is formed when diastase or dilute acids act upon it? 458. Where is cellulose found in nature, and what are its properties? 459. What three compounds may be obtained by the action of nitric acid upon cellulose, and what are they used for? 460. What substances are termed glucosides? Mention some of the more important glucosides.

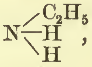
carbon compounds. Organic substances containing nitrogen in the nitric acid form do not occur in nature, but are obtained exclusively by artificial means, generally by treatment of the organic substance with concentrated nitric acid; many of these compounds are more or less explosive, as, for instance, cellulose trinitrate, glyceryl nitrate, and others.

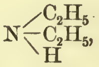
Cyanogen compounds contain nitrogen in the form of cyanogen, CN, a radical the compounds of which will be considered hereafter.

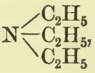
Organic compounds containing nitrogen in the ammonia form are chiefly those known as amines or amides, organic bases or alkaloids. (Albuminous substances also contain nitrogen in the ammonia form).

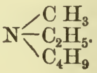
Amines. Whenever the hydrogen of ammonia is replaced by alcoholic radicals (or hydrocarbon residues) compounds are formed which are termed amines. For instance:


$N\begin{cases}H\\H,\\H\end{cases}$


$N\begin{cases}C_2H_5\\H\ ,\\H\end{cases}$


$N\begin{cases}C_2H_5\\C_2H_5,\\H\end{cases}$


$N\begin{cases}C_2H_5\\C_2H_5,\\C_2H_5\end{cases}$


$N\begin{cases}CH_3\\C_2H_5.\\C_4H_9\end{cases}$

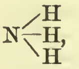
Or

NH_3,	$N(C_2H_5)H_2$,	$N(C_2H_5)_2H$,	$N(C_2H_5)_3$,	$NCH_3.C_2H_5.C_4H_9$.
Ammonia.	Ethylamine.	Diethylamine.	Triethylamine.	Methyl-ethyl-butylamine.

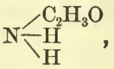
Amines resemble ammonia in their chemical properties; they are, like ammonia, basic substances; they combine with acids directly and without elimination of water, thus:

$$\begin{aligned} NH_3 &+ HCl = NH_4Cl;\\ \underset{\text{Triethylamine.}}{N(C_2H_5)_3} &+ HCl = \underset{\text{Triethylamine chloride.}}{N(C_2H_5)_3HCl.} \end{aligned}$$

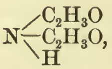
Amides are substances derived from ammonia by replacement of hydrogen atoms by acid radicals. Thus:


$N\begin{cases}H\\H,\\H\end{cases}$

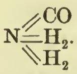
Ammonia.


$N\begin{cases}C_2H_3O\\H\ ,\\H\end{cases}$

Acetamide.


$N\begin{cases}C_2H_3O\\C_2H_3O,\\H\end{cases}$

Diacetamide.


$N\begin{cases}CO\\H_2.\\H_2\end{cases}$

Carbamide or urea.

Amides also resemble ammonia in their chemical properties; to a less extent, however, than amines, because the acid radicals have a tendency to neutralize the basic properties of ammonia:

Formamide, $N(CHO)H_2$, is a colorless liquid, obtained by heating ethyl formate with an alcoholic solution of ammonia. This compound is of interest because it combines with chloral, forming *Chloralformamide* (*Chloralamide*), $N(CHO)H_2.C_2HCl_3O$, a substance recently used as a hypnotic. It is a colorless, odorless, crystalline substance, having a faintly bitter taste. It is soluble in 20 parts of cold water and in 1.5 parts of alcohol. By heating the aqueous solution to 60° C. (140° F.) it is decomposed into chloral and formamide.

Amido-acids are acids in which hydrogen has been replaced by NH_2. Thus, *amido-acetic acid,* also known as *glycocoll* or *glycine,* is represented by the formula $C_2H_3(NH_2)O_2$ or $CH_2\genfrac{<}{}{0pt}{}{NH_2}{CO_2H}$; it is a substance which has both acid and basic properties, and is a product of the decomposition of either glycocholic or hippuric acid by hydrochloric acid.

Amido-formic acid or *carbamic acid,* $CH.NH_2.O_2$, is the acid which, in the form of the ammonium salt, is a constituent of the commercial ammonium carbonate. It is formed by the direct action of carbon dioxide upon ammonia:

$$CO_2 + 2NH_3 = C.NH_4.NH_2\,O_2.$$

Formation of amines and amides. These substances are found as products of animal life (urea), of vegetable life (alkaloids), of destructive distillation (aniline, pyridine), of putrefaction (ptomaines), and may also be produced synthetically—for instance, by the action of ammonia upon the chloride or iodide of an alcohol or acid radical:

$$\underset{\text{Ethyl iodide.}}{C_2H_5.I} + \underset{\text{Ammonia.}}{NH_3} = \underset{\text{Hydriodic acid.}}{HI} + \underset{\text{Ethylamine.}}{NH_2C_2H_5.}$$

$$\underset{\text{Acetyl chloride.}}{C_2H_3O.Cl} + \underset{\text{Ammonia.}}{2NH_3} = \underset{\text{Ammonium chloride.}}{NH_4Cl} + \underset{\text{Acetamide.}}{NH_2.C_2H_3O.}$$

Amines may also be formed by the action of nascent hydrogen upon the cyanides of the alcoholic radicals:

$$\underset{\text{Methyl cyanide.}}{CH_3CN} + 4H = \underset{\text{Ethylamine.}}{NH_2\,C_2H_5.}$$

Amines may in some cases be formed by the action of nascent hydrogen upon nitro-compounds; the manufacture of aniline depends on this decomposition:

$$\underset{\text{Nitro-benzene.}}{C_6H_5NO_2} + \underset{\text{Hydrogen.}}{6H} = \underset{\text{Water.}}{2H_2O} + \underset{\text{Phenylamine, or aniline.}}{NH_2.C_6H_5.}$$

Occurrence of organic bases in nature. The various organic basic substances found in nature are either amines (compounds containing carbon, hydrogen, and nitrogen only), or amides (compounds containing, besides the three elements named, also oxygen). But a small number of organic bases is found in the animal system, urea being the most important one. In plants organic bases are more frequently met with, and are grouped together under the name of *alkaloids.* While the constitution of many alkaloids has not yet been sufficiently explained, we know that many of them are derivatives of aromatic compounds, for which reason the consideration of the whole group will be deferred until benzene and its derivatives are spoken of. The large number of basic substances found in putrefying matter and termed *ptomaines* will also be considered later on.

Cyanogen compounds. Cyanogen itself does not occur in nature, but compounds of it are found in a few plants (amygdalin), and also in some animal fluids (saliva contains sodium sulphocyanate). Gases issuing from volcanoes (or from iron furnaces) sometimes contain cyanogen compounds.

The univalent residue cyanogen, $-C\equiv N$, or CN, was the first compound radical distinctly proved to exist, and isolated by Gay-Lussac in 1814. The name cyanogen signifies "generating blue," in allusion to the various blue colors (Prussian and Turnbull's blue) containing it. (The symbol Cy, sometimes used in place of CN, has been adopted merely to simplify the writing of formulas of cyanogen compounds).

Cyanogen and its compounds show much resemblance to the halogens and their compounds, as indicated by the composition of the following substances:

ClCl, Chlorine,	HCl, Hydrochloric acid.	KI, Potassium iodide.	HClO, Hypochlorous acid.
CNCN, Cyanogen.	HBr, Hydrobromic acid.	KCN, Potassium cyanide.	HCNO, Cyanic acid.
CNCl, Cyanogen chloride.	HCN, Hydrocyanic acid.	AgCN, Silver cyanide.	HCNS, Sulphocyanic acid.

Dicyanogen, $(CN)_2$. The unsaturated radical CN does not exist as such in a free state, but combines whenever liberated with another CN, forming dicyanogen. It may be obtained by heating mercuric cyanide:

$$Hg(CN)_2 = Hg + 2CN.$$

It is a colorless gas, having an odor of bitter almonds, and burning with a purple flame, forming carbon dioxide and nitrogen; it is soluble in water, and may be converted into a colorless liquid by pressure; it acts as a poison, both to animal and vegetable life, even when present in but small proportions in the air.

Hydrocyanic acid, HCN = 27 (*Cyanhydric acid, Hydrogen cyanide, Prussic acid*). This compound is found in the water distilled from the disintegrated seeds or leaves of amygdalus, prunus, laurus, etc. It is also found among the products of the destructive distillation of coal, and is formed by a great number of chemical decompositions. For instance:

By passing ammonia over red-hot charcoal:

$$\underset{\text{Ammonia.}}{4NH_3} + \underset{\text{Carbon.}}{3C} = \underset{\substack{\text{Ammonium}\\\text{cyanide.}}}{2(NH_4CN)} + \underset{\text{Methane.}}{CH_4}.$$

By the action of ammonia on chloroform:

$$\underset{\text{Chloroform.}}{CHCl_3} + NH_3 = \underset{\substack{\text{Hydrocyanic}\\\text{acid.}}}{HCN} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{3HCl}.$$

By heating ammonium formate to 200° C. (392° F.):

$$\underset{\substack{\text{Ammonium}\\\text{formate.}}}{NH_4CHO_2} = \underset{\substack{\text{Hydrocyanic}\\\text{acid.}}}{HCN} + \underset{\text{Water.}}{2H_2O}.$$

By the action of hydrosulphuric acid upon mercuric cyanide:

$$Hg(CN_2) + H_2S = HgS + 2HCN.$$

By the decomposition of alkali cyanides by diluted acids:

$$KCN + HCl = KCl + HCN.$$

By the action of hydrochloric acid upon silver cyanide:

$$AgCN + HCl = AgCl + HCN.$$

By distilling potassium ferrocyanide with diluted sulphuric acid:

$$\underset{\substack{\text{Potassium}\\\text{ferrocyanide.}}}{2K_4Fe(CN)_6} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{6(H_2SO_4)} = \underset{\substack{\text{Potassium ferrous}\\\text{ferrocyanide.}}}{K_2Fe_2(CN)_6} + \underset{\substack{\text{Potassium acid}\\\text{sulphate.}}}{6KHSO_4} + \underset{\substack{\text{Hydrocyanic}\\\text{acid.}}}{6HCN}.$$

Experiment 55. Place 20 grammes of potassium ferrocyanide and 40 c.c. of water into a boiling-flask of about 200 c.c. capacity; provide the flask with a funnel-tube and connect it with a suitable condenser, the exit of which should dip into 60 c.c. of diluted alcohol, contained in a receiver, which latter should be kept cold by ice during the operation. After having ascertained that all the joints are tight, add through the funnel-tube a previously prepared mixture of 15 grammes of sulphuric acid and 20 c.c. of water. Apply heat and slowly distil until there is little liquid left with the salts remaining in the flask.

Determine the strength of the alcoholic solution of hydrocyanic acid thus prepared volumetrically and dilute it with water until it contains exactly two per cent. of HCN.

Pure hydrocyanic acid is, at a temperature below 26° C. (78.8° F.), a colorless, mobile liquid, of a penetrating, characteristic odor resembling that of bitter almonds; it boils at 26.5° C. (80° F.) and crystallizes at —15° C. (5° F.). It is readily soluble in water, and a 2 per cent. solution is the *diluted hydrocyanic acid, Acidum hydrocyanicum dilutum.*

According to the U. S. P., this diluted acid is made either by the decomposition of potassium ferrocyanide by diluted sulphuric acid in a retort, the delivery-tube of which passes into a receiver containing water, by which the liberated gas is absorbed, this liquid being afterward diluted with a sufficient quantity of water to make a 2 per cent. solution, or it is made extemporaneously by the decomposition of 6 parts by weight of silver cyanide by 5 parts of hydrochloric acid, diluted with 55 parts of water, allowing the silver chloride to subside and pouring off the clear liquid.

The diluted acid has the characteristic odor of bitter almonds, a slightly acid reaction, and is completely volatilized by heating. Whilst the pure acid is very readily decomposed by exposure to light, etc., the dilute acid is fairly stable.

Potassium cyanide, Potassii cyanidum, $KCN = 65$. The pure salt may be obtained by passing hydrocyanic acid into an alcoholic solution of potassium hydroxide. The commercial article, however, is a mixture of potassium cyanide with potassium cyanate. It is obtained by fusing potassium ferrocyanide with potassium carbonate in a crucible, when potassium cyanide and cyanate are formed, whilst carbon dioxide escapes, and metallic iron is set free and collects on the bottom of the crucible. The decomposition is as follows:

$$\underset{\substack{\text{Potassium}\\\text{ferrocyanide.}}}{K_4Fe(CN)_6} + \underset{\substack{\text{Potassium}\\\text{carbonate.}}}{K_2CO_3} = \underset{\substack{\text{Potassium}\\\text{cyanide.}}}{5KCN} + \underset{\substack{\text{Potassium}\\\text{cyanate.}}}{KCNO} + \underset{\text{Iron.}}{Fe} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2}.$$

Potassium cyanide, U. S. P., should contain at least 90 per cent. of the pure salt; it is a white, deliquescent substance, odorless when perfectly dry, but emitting the odor of hydrocyanic acid when moist; it is soluble in about 2 parts of water; this solution has an alkaline reaction and decomposes slowly in the cold, but rapidly on heating, with the formation of potassium and ammonium carbonates:

$$2KCNO + 4H_2O = K_2CO_3 + (NH_4)_2CO_3.$$

Potassium cyanides and other alkali cyanides show a tendency to combine with the cyanides of heavy metals, forming a number of double cyanides, such as the cyanide of sodium and silver, $NaCN.AgCN$, etc.

Silver cyanide, Argenti cyanidum, $AgCN = 133.7$ (*Cyanide of silver*). A white powder, obtained by precipitating solution of potassium cyanide with silver nitrate. It is insoluble in water, slowly soluble in water of ammonia; evolves cyanogen when heated, metallic silver being left.

Mercuric cyanide, Hydrargyri cyanidum, $Hg(CN)_2$. A white crystalline salt, obtained by dissolving mercuric oxide in hydrocyanic acid; it is soluble in water and alcohol and evolves cyanogen when heated.

Analytical reactions for hydrocyanic acid.

(Potassium cyanide, KCN, may be used.)

1. Hydrocyanic acid, or soluble cyanides, give with silver nitrate a white precipitate of silver cyanide, which is sparingly soluble in ammonia, soluble in alkali cyanides or thiosulphates, but insoluble in diluted nitric acid. Concentrated nitric acid dissolves it with decomposition:

$$HCN + AgNO_3 = AgCN + HNO_3.$$

2. Hydrocyanic acid mixed with ammonium hydric sulphide and evaporated to dryness forms sulphocyanic acid, which, upon being slightly acidulated with hydrochloric acid, gives with ferric chloride a blood-red color of ferric sulphocyanate. (Excess of ammonium sulphide must be avoided.)

3. Hydrocyanic acid, or soluble cyanides, give, when mixed with ferrous and ferric salts and potassium hydroxide, a greenish precipitate, which, upon being dissolved in hydrochloric acid, forms a precipitate of Prussian blue, $Fe_4(FeC_6N_6)_3$. This reaction depends on the formation of potassium ferrocyanide by the action of the cyanogen upon both the potassium of the potassium hydroxide and the iron of the ferrous salt. In alkaline solutions, the blue precipitate does not form, for which reason hydrochloric acid is added.

4. Hydrocyanic acid heated with dilute solution of picric acid gives a deep-red color on cooling.

In cases of poisoning, the matter under examination is distilled (if necessary after the addition of water) from a retort connected with a cooler. To the distilled liquid the above tests are applied. If the substance under examination should have an alkaline or neutral reaction, the addition of some sulphuric acid may be necessary in order to liberate the hydrocyanic acid. The objectionable feature to this acidifying is the fact that non-poisonous potassium ferrocyanide might be present, which upon the addition of sulphuric acid would liberate hydrocyanic acid. In cases where the addition of an acid becomes necessary, a preliminary examination should, therefore, decide whether or not ferro- or ferricyanides are present.

Antidotes. Hydrocyanic acid is a powerful poison both when inhaled or swallowed in the form of the acid or of soluble cyanides. As an antidote is recommended a mixture of ferrous sulphate and ferric chloride with either sodium carbonate or magnesia. The action of this mixture is explained in the above reaction 3, the object being to convert the soluble cyanide into an insoluble ferrocyanide of iron. In most cases of poisoning by hydrocyanic acid there is, however, no time for the action of such an antidote, in consequence of the rapidity of the action of the poison, and the treatment is chiefly directed to the maintenance of respiration by artificial means.

Cyanic acid, $HCNO$, and Sulphocyanic acid, $HCNS$, are both colorless acid liquids, the salts of which are known as *cyanates* and *sulpho-cyanates.* These salts are obtained from alkali cyanides by treating them with oxidizing agents or by boiling their solutions with sulphur, when either oxygen or sulphur is taken up by the alkali cyanide:

$$KCN + O = KCNO = \text{Potassium cyanate.}$$
$$KCN + S = KCNS = \text{Potassium sulphocyanate.}$$

The acids themselves may be liberated from their salts by dilute mineral acids. Sulphocyanates give with ferric salts a deep-red color, which is not affected by hydrochloric acid, but disappears on the addition of mercuric chloride.

Metallocyanides. Cyanogen not only combines with metals to form the true cyanides, which may be looked upon as derivatives of hydrocyanic acid, but cyanogen also enters into combination with certain metals (chiefly iron), forming a number of complex radicals, which upon combining with hydrogen form acids, or with basic elements form salts. It is a characteristic feature of the compound cyanogen radicals, thus formed, that the analytical characters of the metals (iron, etc.) entering into the radical are completely hidden. Thus, the iron in ferro- or ferricyanides is not precipitated by either alkalies, soluble carbonates, ammonium sulphide, or any of the common reagents for iron, and its presence can only be demonstrated by these reagents after the organic nature of the compound has been destroyed by burning it (or otherwise), when ferric oxide is left, which may be dissolved in hydrochloric acid and tested for in the usual manner.

The principal iron-cynogen radicals are *ferrocyanogen* $[Fe^{ii}(CN)_6^{i}]^{iv}$, and *ferricyanogen* $[Fe_2^{vi}(CN)_{12}^{i}]^{vi}$. These two radicals contain iron in the ferrous and ferric state respectively, and form, upon combining with hydrogen, acids which are known as *hydroferrocyanic acid,* $H_4Fe(CN)_6$ (tetrabasic), and *hydroferricyanic acid,* $H_6Fe_2(CN)_{12}$ (hexabasic); the salts of these acids are termed ferrocyanides and ferricyanides.

Potasssium ferrocyanide, Potassii ferrocyanidum, $K_4Fe(CN)_6.3H_2O = 421.9$ (*Yellow prussiate of potash*). This salt is manufactured on a large scale by heating refuse animal matter (waste leather, horns, hoofs, etc.) with potassium carbonate and iron (filings, etc.). The fused mass is boiled with water, and from the solution thus formed the crystals separate on cooling.

The nitrogen and carbon of the organic matter (heated as above stated) combine, forming cyanogen, which enters into combination first with potassium and afterward with iron.

Potassium ferrocyanide forms large, translucent, pale lemon-yellow, soft, odorless, non-poisonous, neutral crystals, easily dissolving in water, but insoluble in alcohol.

Analytical reactions:

1. Ferrocyanides heated on platinum foil burn and leave a residue of (or containing) ferric oxide.

2. Ferrocyanides heated with concentrated sulphuric acid evolve carbonic oxide; with dilute sulphuric acid liberate hydrocyanic acid; with concentrated hydrochloric acid liberate hydroferrocyanic acid.

3. Soluble ferrocyanides give a blue precipitate with ferric salts (Plate I., 5):

$$\underset{\substack{\text{Potassium}\\\text{ferrocyanide.}}}{3K_4Fe(CN)_6} + \underset{\substack{\text{Ferric}\\\text{chloride.}}}{2Fe_2Cl_6} = \underset{\substack{\text{Potassium}\\\text{chloride.}}}{12KCl} + \underset{\substack{\text{Ferric ferro-}\\\text{cyanide.}}}{Fe_4(FeC_6N_6)_3}.$$

The blue precipitate of ferric ferrocyanide, or *Prussian blue*, is insoluble in water and diluted acids, soluble in oxalic acid (blue ink), and is decomposed by alkalies with separation of brown ferric hydroxide and formation of potassium ferrocyanide. The addition of an acid restores the blue precipitate.

4. Soluble ferrocyanides give with cupric solutions a brownish-red precipitate of cupric ferrocyanide. (Plate III., 5.)

5. Soluble ferrocyanides produce, with solutions of silver, lead, and zinc, white precipitates of the respective ferrocyanides.

6. Ferrocyanides give with ferrous salts a white precipitate of ferrous ferrocyanide, soon turning blue by absorption of oxygen. (Plate I., 4.)

Potassium ferricyanide, $K_6Fe_2(CN)_{12}$ (*Red prussiate of potash*). Obtained by passing chlorine through solution of potassium ferrocyanide:

$$\underset{\substack{\text{Potassium}\\\text{ferrocyanide.}}}{2K_4Fe(CN)_6} + \underset{\text{Chlorine.}}{2Cl} = \underset{\substack{\text{Potassium}\\\text{chloride.}}}{2KCl} + \underset{\substack{\text{Potassium}\\\text{ferricyanide.}}}{K_6Fe_2(CN)_{12}}.$$

While apparently this decomposition consists merely in a removal of two atoms of potassium from two molecules of potassium ferrocyanide, the change is actually more complete, as the atoms arrange themselves differently, the iron passing also from the ferrous to the ferric state.

Potassium ferricyanide crystallizes in red prisms, soluble in water. It forms, with ferrous solutions, a blue precipitate of ferrous ferricyanide, or *Turnbull's blue*:

$$K_6Fe_2(CN)_{12} + 3FeSO_4 = 3K_2SO_4 + Fe_3Fe_2(CN)_{12}.$$

With ferric solutions no precipitate is produced by potassium ferricyanide, but the color is changed to a deep brown.

Nitro-cyan-methane, $CH_2.CN.NO_2$ (*Fulminic acid*). This substance may be looked upon as a derivative of methane, CH_4, in which two atoms of hydrogen are replaced by cyanogen and NO_2 respectively. It is not known in the separate state, but its combinations with metals are well known, especially *mercuric fulminate*, which is manufactured and used as an explosive in percussion caps, etc. It is made by adding alcohol to a solution of mercury in nitric acid. Silver fulminate can be obtained by a similar process.

48. BENZENE SERIES. AROMATIC COMPOUNDS.

General remarks. It has been stated before that all organic compounds may be looked upon as derivatives of either methane, CH_4, or benzene, C_6H_6, these derivatives being often spoken of as fatty and aromatic compounds respectively. The term aromatic compounds was given to these substances on account of the peculiar and fragrant odor possessed by many, though not by all of them. Benzene and

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QUESTIONS. 461. What are the three chief forms in which nitrogen enters into organic compounds? 462. What are amines and amides; in what respects do they resemble ammonia compounds? 463. What is cyanogen, what is dicyanogen, and how is the latter obtained? 464. How does cyanogen occur in nature, and which non-metallic elements does it resemble in the constitution of various compounds? 465. Mention some reactions by which hydrocyanic acid is formed, and state the two processes by which the official diluted acid is obtained. What strength and what properties has this acid? 466. State the composition of pure potassium cyanide and of the commercial article. How is the latter made? 467. Give reactions for hydrocyanic acid and cyanides. 468. Explain the constitution and give the composition of ferro- and ferricyanides. 469. Give composition, mode of manufacture, and tests of potassium ferrocyanide. 470. What is red prussiate of potash, how is it obtained, and by what reactions can it be distinguished from the yellow prussiate?

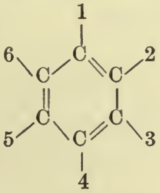
methane derivatives differ considerably in many respects, and, as a general rule, aromatic compounds cannot be converted into fatty compounds, or the latter into aromatic compounds, without suffering the most vital decomposition of the molecule, and in many cases this transformation cannot be accomplished at all.

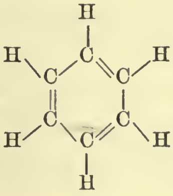
On the average, aromatic compounds are richer in carbon than fatty compounds, containing of this element at least 6 atoms; when decomposed by various methods, aromatic compounds, in many cases, yield benzene as one of the products; most aromatic substances have antiseptic properties, and none of them serves as animal food, although quite a number are taken into the system in small quantities, as, for instance, some essential oils, caffeine, etc.

While some aromatic compounds are products of vegetable life, many of them (like benzene itself) are obtained by destructive distillation, and are, therefore, contained in coal-tar, from which quite a number are separated by fractional distillation.

The constitution of benzene is best explained by assuming that of the 4 × 6 = 24 affinities of the 6 carbon atoms, 18 affinities are lost by uniting the carbon atoms into a closed chain, while but 6 affinities are left unprovided for and may be saturated by other elements or groups of elements.

The carbon chain of aromatic compounds and benzene may be graphically represented thus:

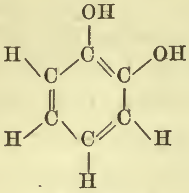


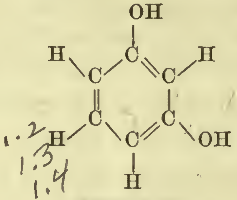


It has been found that whenever *one* atom or *one* radical replaces hydrogen in benzene, the product obtained is the same, no matter by what method the change is brought about. Thus we know but *one* mono-brom-benzene, C_6H_5Br, *one* nitro-benzene, $C_6H_5NO_2$, etc.

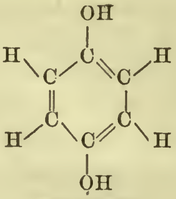
It is different when two or more atoms or radicals (of the same kind) replace hydrogen in benzene, since it has been found that in this case often isomeric compounds are formed.

For instance, we know three different substances which have been obtained by replacement of two hydrogen atoms in benzene by two hydroxyl groups. This would indicate that it makes a difference, as far as the properties of a compound are concerned, in which relative position the introduced radicals stand to one another, and while we have no proof whatever in regard to this position, yet we often represent it graphically, as, for instance, in the following three cases, where the two groups OH replace hydrogen in different positions:


Ortho-position.
1.2.



Meta-position.
1.3.


Para-position.
1.4.

Designating the hydrogen atoms in benzene with numbers, thus: $C_6\overset{1}{H}\overset{2}{H}\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$, the above 3 compounds show that in one case the hydrogen atoms 1 and 2, in the second 1 and 3, in the third 1 and 4 have been replaced by OH. The compounds formed in this way are distinguished as ortho-, meta-, and para-compounds.

The molecular formula of the above three compounds is $C_6H_6O_2$, apparently indicating benzene in combination with two atoms of oxygen or dioxybenzene; actually they are dihydroxy benzene. *Ortho*-dihydroxy benzene, $C_6H_4\overset{1}{O}H\overset{2}{O}H$, is known as pyro-catechin, *meta*-dihydroxy benzene, $C_6H_4\overset{1}{O}H\overset{3}{O}H$, as resorcin, and *para*-dihydroxy benzene, $C_6H_4\overset{1}{O}H\overset{4}{O}H$, as hydroquinone.

Benzene series of hydrocarbons. By replacing the hydrogen atoms in benzene by methyl, CH_3, a series of hydrocarbons is formed having the general composition C_nH_{2n-6}. To this benzene series belong:

				B. P.
Benzene . . .	C_6H_6	=	....	80° C.
Toluene . . .	C_7H_8	=	$C_6H_5CH_3$	110
Xylene . . .	C_8H_{10}	=	$C_6H_4(CH_3)_2$	142
Cumene . . .	C_9H_{12}	=	$C_6H_3(CH_3)_3$	151
Cymene . . .	$C_{10}H_{14}$	=	$(C_6H_2(CH_3)_4$?	175
Penta-methyl-benzene	$C_{11}H_{16}$	=	$C_6H(CH_3)_5$	188
Hexa-methyl-benzene	$C_{12}H_{18}$	=	$C_6(CH_3)_6$	202

The first four members of this series are found in coal-tar; the fifth member, cymene, $C_{10}H_{14}$, occurs in the oil of thyme; the last two have been obtained by synthetical processes. While but one toluene is known, the higher members form quite a number of isomeric compounds. Cymene, found in the oil of thyme, is, for instance, not the tetra-methyl-benzene, but the para-methyl-propyl-benzene, $C_6H_4\,CH_3.C_3H_7$. This compound is of interest on account of its close relation to the terpenes and camphors, which will be spoken of later.

Benzene, C_6H_6 (*Benzol*). When coal-tar is distilled, products are obtained which are either lighter or heavier than water, and by collecting the distillate in water a separation into so called *light oil* (floating on the water) and *heavy oil* (sinking beneath the water) is accomplished. Benzene is found in the light oil and obtained from it by distillation after phenol has been removed by treatment with caustic soda and some basic substances by means of sulphuric acid. Pure benzene may be obtained by heating benzoic acid with calcium hydroxide:

$$C_6H_5.CO_2H + Ca(OH)_2 = CaCO_3 + H_2O + C_6H_6.$$

Experiment 56. Mix 25 grammes of benzoic acid with 40 grammes of slaked lime and distil from a dry flask, connected with a condenser. Add to the distilled fluid a little calcium chloride and redistil from a small flask. The product obtained is pure benzene. Notice that it solidifies when placed in a freezing mixture of ice and common salt. Observe the analogy between Experiments 56 and 40. In one case a fatty acid is decomposed by an alkali with liberation of methane, in the other an aromatic acid with liberation of benzene, the carbonate of the decomposing hydroxide being formed in both cases.

Pure benzene is a colorless, highly volatile liquid, having a peculiar, aromatic odor and a specific gravity of 0.884; it boils at 80.5° C. (177° F.) and solidifies at 0° C. (32° F.); it is an excellent solvent for fats, oils, resins, and many other organic substances.

Nitro-benzene, $C_6H_5.NO_2$. When benzene is treated with concentrated nitric acid, or with a mixture of nitric and sulphuric acids, nitro-benzene is formed:

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O.$$

Experiment 57. Mix 50 c.c. of sulphuric acid with 25 c.c. nitric acid; allow to cool, place the vessel containing the mixture in water, and add gradually 5 c.c. of benzene, waiting after the addition of a few drops each time until the reaction is over. Shake well until all benzene is dissolved and pour the liquid into 300 c.c. of water. The yellow oil which sinks to the bottom is nitro-benzene. It may be purified by washing with water and redistilling, after removal of water and shaking with calcium chloride.

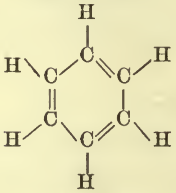
Nitro-benzene is an almost colorless or yellowish oily liquid, which is insoluble in water, has a specific gravity of 1.2, a boiling-point of 205° C. (401° F.), a sweetish taste, highly poisonous properties, even when inhaled, and an odor resembling that of oil of bitter almond, for which it is substituted under the name of *essence of mirbane.* It is manufactured on a large scale and used chiefly in the preparation of aniline, for which see Index.

Benzene-derivatives. The relation existing between methane- and benzene-derivatives may be shown by comparing the composition of a few derivatives :

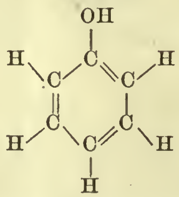
Methane,	CH_4	Benzene,	C_6H_6
Methyl,	CH_3	Benzyl, Phenyl,	$\left.\right\} C_6H_5$
Ethane, Methyl-methane,	$\left.\right\} CH_3.CH_3$	Toluene, Methyl-benzene,	$\left.\right\} C_6H_5.CH_3$
Methyl-hydroxide, Methyl-alcohol,	$\left.\right\} CH_3OH$	Phenyl-hydroxide, Phenol,	$\left.\right\} C_6H_5.OH$
Glycerin,	$C_3H_5 \begin{array}{l} / OH \\ - OH \\ \backslash OH \end{array}$	Pyrogallol,	$C_6H_3 \begin{array}{l} / OH \\ - OH \\ \backslash OH \end{array}$
Acetic acid,	$CH_3.CO_2H$	Benzoic acid,	$C_6H_5.CO_2H$
Acetic aldehyde,	$CH_3.COH$	Benzoic aldehyde,	$C_6H_5.COH$
Ethyl-sulphonic acid,	$SO_2 \begin{array}{l} / C_2H_5 \\ \backslash OH \end{array}$	Benzene-sulphonic acid,	$SO_2 \begin{array}{l} / C_6H_5 \\ \backslash OH \end{array}$
Malonic acid,	$CH_2 \begin{array}{l} / CO_2H \\ \backslash CO_2H \end{array}$	Phtalic acid,	$C_6H_4 \begin{array}{l} / CO_2H \\ \backslash CO_2H \end{array}$
Tartaric acid,	$C_2H_2 \begin{array}{l} / 2OH \\ \backslash 2CO_2H \end{array}$	Salicylic acid,	$C_6H_4 \begin{array}{l} / OH \\ \backslash CO_2H \end{array}$
Ethyl ether,	$\left\{ \begin{array}{l} C_2H_5 \backslash \\ C_2H_5 / \end{array} \right. O$	Phenyl-ether,	$\left\{ \begin{array}{l} C_6H_5 \backslash \\ C_6H_5 / \end{array} \right. O$
Methyl-ethyl ether,	$\left\{ \begin{array}{l} C\,H_3 \backslash \\ C_2H_5 / \end{array} \right. O$	Methyl-phenyl ether, anisol,	$\left\{ \begin{array}{l} C\,H_3 \backslash \\ C_6H_5 / \end{array} \right. O$

The following graphic formulas may serve to illustrate the constitution of some aromatic compounds :

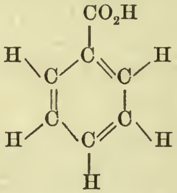
Hydrocarbons. *Alcohols.* *Acids.*



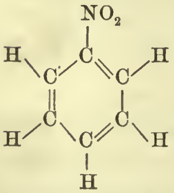
Benzene, C_6H_6.



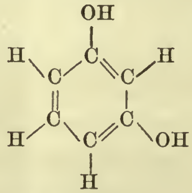
Phenol or carbolic acid, $C_6H_5.OH$.



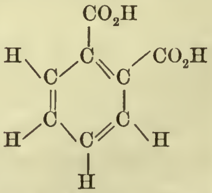
Benzoic acid, $C_6H_5.CO_2H$.



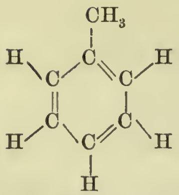
Nitro-benzene, $C_6H_5NO_2$.

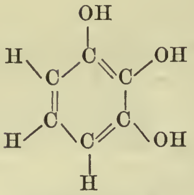


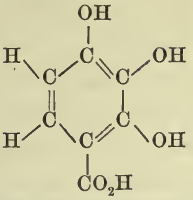
Resorcin, $C_6H_4(OH)_2$.

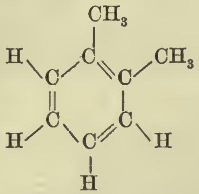


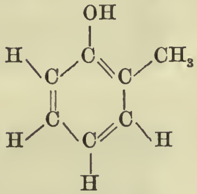
Phtalic acid, $C_6H_4(CO_2H)_2$.

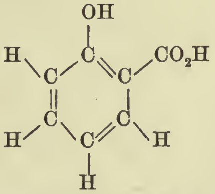

Toluene, methyl-benzene, $C_6H_5.CH_3$.

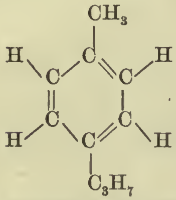

Pyrogallol, $C_6H_3(HO)_3$.

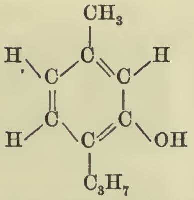

Gallic acid, $C_6H_2.CO_2H.(OH)_3$.

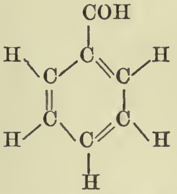

Xylene, di-methyl-benzene, $C_6H_5.(CH_3)_2$.


Cresol, $C_6H_4.CH_3.OH$.


Salicylic acid, $C_6H_4.CO_2H.OH$.


Cymene, methyl-propyl benzene, $C_6H_4.CH_3.C_3H_7$.


Thymol, $C_6H_3CH_3.C_3H_7.OH$.


Benzaldehyde, oil of bitter almond, $C_6H_5.COH$.

The preceding graphic formulas show in the first column (besides nitro-benzene) a number of hydrocarbons, in the second column alcohols (or phenols), obtained by introducing hydroxyl into the hydrocarbon molecule, and in the third column chiefly aromatic acids, formed by introducing carboxyl, CO_2H, or carboxyl and hydroxyl.

Phenols. While the term phenol is generally used for carbolic acid, it also belongs to that class of substances which we may call aromatic alcohols. According to the number of hydrogen atoms replaced by hydroxyl, we find mon-atomic, di-atomic, and tri-atomic phenols, corresponding to the similarly constituted alcohols. Phenols differ from common alcohols in not yielding aldehydes or acids by oxidation.

Carbolic acid, Acidum carbolicum, $C_6H_5OH = 94$ (*Phenol, Phenyl hydrate, Phenyl alcohol*). Crude carbolic acid is a liquid obtained during the distillation of coal-tar between the temperatures of 170°–190° C. (338°–374° F.), and containing chiefly phenol, besides cresol, C_7H_7OH, and other substances. It is a reddish-brown liquid of a strongly empyreumatic and disagreeable odor.

By fractional distillation of the crude carbolic acid, the pure acid is obtained, which forms colorless, interlaced, needle-shaped crystals, sometimes acquiring a pinkish tint; it has a characteristic, slightly aromatic odor, is deliquescent in moist air, soluble in from 15 to 20 parts of water, and very soluble in alcohol, ether, chloroform, glycerin, fat and volatile oils, etc.; it has, when diluted, a sweetish and afterward burning, caustic taste; it produces a benumbing and caustic effect, and even blisters on the skin; it is strongly poisonous, and a powerful antiseptic agent, preventing fermentation and putrefaction to a marked degree; fusing-point about 35° C. (95° F.), boiling-point 188° C. (370° F.), specific gravity 1.065.

Phenol, though generally called carbolic acid, has a neutral or but faintly acid reaction, and the constitution of an alcohol, but it readily combines with strong bases, for instance, with sodium, forming sodium phenoxide or sodium phenolate:

$$C_6H_5OH + NaOH = C_6H_5ONa + H_2O.$$

Phenol obtained by synthetical processes is now sold in a state of great purity; it has comparatively little odor.

As *antidotes* may be used olive oil or castor oil, a mixture of both, or a mixture of magnesia and oil.

Tests for carbolic acid.

(Use an aqueous solution.)

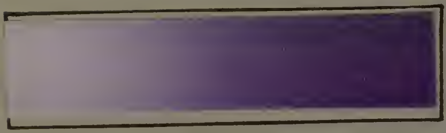
1. It coagulates albumin and collodion.
2. It colors solutions of neutral ferric chloride intensely and permanently violet-blue. (Plate VI., 1.)
3. Bromine water produces, even in dilute solutions, a white precipitate of tri-brom-phenol, $C_6H_2Br_3OH$.
4. A fresh-cut slip of pinewood moistened with carbolic acid, and then exposed to hydrochloric acid fumes, turns blue on exposure to sunlight.
5. On heating with nitric acid it turns yellow, picric acid being formed.

Creosote, Creosotum. This is a liquid product of the distillation of wood-tar, especially of beechwood-tar, which contains sometimes as much as 25 per cent. of creosote; it resembles carbolic acid in many respects, especially in its antiseptic properties and its action

PLATE VI.

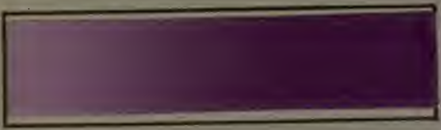
BENZENE DERIVATIVES.

1



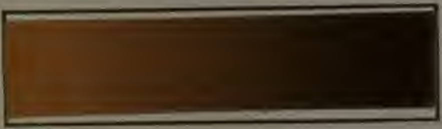
Carbolic acid with ferric chloride.

2



Salicylic acid with ferric chloride.

3

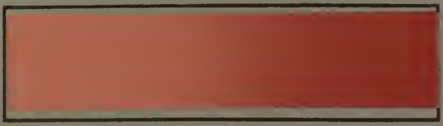


Pyrogallic acid with alcoholic solution of potassium hydroxide.

4

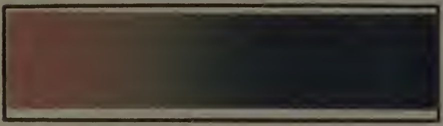
Gallotannic acid, precipitated by ferric chloride and precipitate dissolved in excess of tannic acid.

5



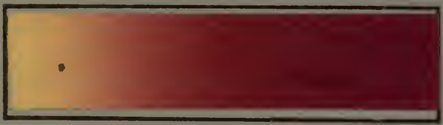
Santonin with alcoholic solution of potassium hydroxide.

6



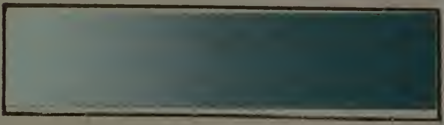
Acetanilid treated successively with hydrochloric acid, carbolic acid, bleaching powder, and ammonia water.

7



Antipyrine treated with nitric acid.

8



Antipyrine with solution of sodium nitrite and acetic acid.

on the skin. It is a mixture of substances, but consists chiefly of creosol, $C_8H_{10}O_2$, and guaiacol, $C_7H_8O_2$.

From carbolic acid creosote may be distinguished by not coagulating albumin and collodion, by not being solidified on cooling, by not coloring ferric chloride permanently, and by its boiling-point, which rises from 205° to 215° C. (401° to 419° F.).

Sulphocarbolic acid, $HSO_3.C_6H_4.OH$ (*Phenol-sulphonic acid, Sozolic acid, Aseptol*). Formed by dissolving carbolic acid in strong sulphuric acid:

$$C_6H_5OH + H_2SO_4 = HC_6H_5SO_4 + H_2O.$$

Sodium Sulphocarbolate, Sodii sulphocarbolas, $NaSO_3.C_6H_4.OH + 2H_2O$, is obtained as a white soluble salt by dissolving sodium carbonate in the above acid.

Sulphonic acid has been spoken of before, when it was shown that mercaptans are converted into compounds termed sulphonic acids. These acids may be looked upon as derivatives of sulphurous acid, obtained from it by replacement of hydrogen by radicals. The relation existing between carbonic and sulphonic acids may be represented by the following formulas:

Carbonic acid,	$CO\left\langle\begin{matrix}OH\\OH\end{matrix}\right.$	Sulphuric acid,	$SO_2\left\langle\begin{matrix}OH\\OH\end{matrix}\right.$
Formic acid,	$CO\left\langle\begin{matrix}H\\OH\end{matrix}\right.$	Sulphurous acid,	$SO_2\left\langle\begin{matrix}H\\OH\end{matrix}\right.$
Acetic acid,	$CO\left\langle\begin{matrix}CH_3\\OH\end{matrix}\right.$	Methyl-sulphonic acid,	$SO_2\left\langle\begin{matrix}CH_3\\OH\end{matrix}\right.$
Any compound carbonic acid,	$CO\left\langle\begin{matrix}R\\OH\end{matrix}\right.$	Any sulphonic acid,	$SO_2\left\langle\begin{matrix}R\\OH\end{matrix}\right.$

According to this view, the above sulphocarbolic acid is actually phenol-sulphonic acid, its constitution being represented by the formula, $SO_2\left\langle\begin{matrix}C_6H_5O\\OH\end{matrix}\right.$.

Ichthyol, Sodium ichthyo-sulphonate, $C_{26}H_{36}S_3Na_2O_6$. Ichthyol is the sodium or ammonium salt of a complex sulphonic acid, obtained by the dry distillation of a bituminous mineral found in Tyrol. It is a brown, tar-like liquid, having a disagreeable odor.

Picric acid, $C_6H_2(NO_2)_3OH$ (*Trinitro-phenol, Carbazotic acid*). This substance is formed by the action of nitric acid on various matters (silk, wool, indigo, Peruvian balsam, etc.), and is manufactured on a large scale by slowly dropping carbolic acid into fuming nitric acid. Picric acid forms yellow crystals, which are sparingly soluble in water; it has a very bitter taste, strongly poisonous properties, and is used as a yellow dye for silk and wool, and as a reagent for albumin. While carbolic acid has but slight acid properties, picric acid behaves like a strong acid, forming salts known as picrates, most of which are explosive.

Phenacetin, Para-acetphenetidin, $C_6H_4.O(C_2H_5).NH(C_2H_3O)$. When mononitrophenol, $C_6H_4.NO_2.OH$, is treated with reducing agents, the oxygen of NO_2 is replaced by hydrogen, and *amido-phenol*, $C_6H_4.OH.NH_2$, is formed. The methyl ether of this compound, $C_6H_4.O(CH_3).NH_2$, is known as *anisidin*, and the ethyl ether, $C_6H_4.O(C_2H_5).NH_2$, as *phenetidin*. By the action of glacial acetic acid upon para-phenetidin, one hydrogen atom in NH_2 is replaced by acetyl, C_2H_3O, when para-acetphenetidin is formed. The compound is used as an antipyretic under the name of phenacetin.

It is a colorless, odorless, tasteless powder, sparingly soluble in water, readily soluble in alcohol; it fuses at 135° C. (275° F.). Fresh chlorine water colors a hot aqueous solution first violet, then ruby-red. The same color is obtained by boiling 0.1 gramme of phenacetin with 1 c.c. of hydrochloric acid for one minute, diluting with 10 c.c. of water, filtering when cold, and adding 3 drops of solution of chromic acid.

Resorcin, Resorcinum, $C_6H_4(OH)_2$ (*Resorcinol, Meta-dihydroxybenzene*). The formula indicates that this compound is a di-atomic phenol. It is formed by fusing different resins, such as galbanum, asafœtida, etc., with caustic alkalies, but it is also obtained synthetically from benzene.

Resorcin is a white, or faintly-reddish, crystalline powder, having a somewhat sweetish taste and a slightly aromatic odor; it fuses at 118° C. (244° F.), boils at 276° C. (529° F.), and is soluble in less than its own weight of water. A dilute solution gives with ferric chloride a bluish-violet color. Resorcin, when heated for a few minutes with phtalic acid in a test-tube, forms a yellowish-red mass, which, when added to a dilute solution of caustic soda, forms a highly fluorescent solution. Other fluorescent compounds are obtained by heating resorcin with very little sulphuric and either citric, oxalic, or tartaric acid, dissolving in a mixture of water and alcohol and supersaturating the solution with ammonia. Resorcin is largely used in the manufacture of certain dyes.

Cymene, $C_{10}H_{14}$ or $C_6H_4.CH_3.C_3H_7$ (*Para-methyl-propyl-benzene*). This hydrocarbon occurs in the oil of thyme and in the volatile oils of a few other plants; it has also been made synthetically; it is a liquid of a pleasant odor, boiling at 175° C. (347° F.).

Cymene is of special interest, because it is closely related to the terpenes and camphors, from all of which it may be obtained by comparatively simple processes.

Terpenes, $C_{10}H_{16}$. This term is applied to the various isomeric hydrocarbons of the composition $C_{10}H_{16}$, which are often looked upon as compounds formed by direct addition of hydrogen to cymene.

Terpenes are the chief constituents of a large number of essential oils, such as oil of turpentine, juniper, lemon, rosemary, bergamot, lavender, etc. Terpenes are readily acted upon by many agents, and hence undergo numerous changes. One of these changes is polymerization—*i. e.*, conversion into compounds of the composition $C_{15}H_{24}$ and $C_{20}H_{32}$, which may be effected by heating a terpene in a sealed tube, or by shaking it with concentrated sulphuric acid or with certain other substances. Oxygen and hydrochloric acid combine directly with terpenes; dilute nitric acid oxidizes them readily with the formation of a number of organic acids; bromine and iodine convert them into cymene.

Oil of turpentine, $C_{10}H_{16}$, is the terpene most largely used. It is a thin, colorless liquid of a characteristic aromatic odor, and an acrid, caustic taste; it is insoluble in water, soluble in alcohol, and an excellent solvent for resins and many other substances. When treated with hydrochloric acid gas direct combination takes place and a white solid substance of the composition $C_{10}H_{16}HCl$ is formed, which is known as terpene hydrochloride, or *artificial camphor*, on account of its similarity to camphor both in appearance and odor.

Experiment 58. Through 10 or 20 c.c. of oil of turpentine pass a current of hydrochloric acid gas for some time, or until a quantity of a solid substance has separated. Collect this substance, which is artificial camphor, upon a filter; notice its characteristic odor. Heat some of it; hydrochloric acid is set free.

Terebene, $C_{10}H_{16}$, is the optically inactive modification of terpene, obtained from oil of turpentine by mixing it with sulphuric acid, distilling, washing the distilled oil with soda solution, redistilling and collecting the portions which pass over at a temperature of 156° to 160° C. (313° to 320° F.). Terebene resembles oil of turpentine in most respects, but has not the unpleasant odor of this oil.

Resins are obtained, together with the essential oils, from plants. Mixtures of a resin and a volatile oil are known as *oleo-resins*, while mixtures of a resin or oleo-resins and gum are known as *gum-resins*. The name *balsam* is also used for a certain group of oleo-resins.

The resins are mostly amorphous, brittle bodies, insoluble in water, but soluble in alcohol, ether, fatty and essential oils; they are fusible, but decompose before being volatilized; they all contain oxygen and exhibit somewhat acid properties.

Turpentine, the oleo-resin of the conifers, contains besides the oil of turpentine a resin called *colophony, rosin*, or *ordinary resin*, consisting chiefly of the anhydride of *abietic acid*, $C_{44}H_{64}O_5$.

Copaiva balsam consists of a volatile oil and a resin, the latter being principally copaivic acid, $C_{20}H_{30}O_2$.

Of fossil resins may be mentioned *amber* and *asphalt*, the latter having most likely been formed from petroleum.

India-rubber, Elastica (*Caoutchouc*), is the dried milky juice found in quite a number of trees growing in the tropics. The principal constituents are hydrocarbons of the composition $C_{20}H_{32}$, $C_{10}H_{16}$, and C_5H_8. The commercial article is yellowish-brown, has a specific gravity of 0.92 to 0.94, is soft, flexible, insoluble in water and alcohol, but soluble in carbon disulphide, ether, chloroform, and benzene. It is not acted upon by dilute mineral acids; concentrated nitric and sulphuric acid, as well as chlorine, attack it after a time. It is hard and tough in the cold; when heated it becomes viscous at 125° C. (257° F.), and fuses at 170°–180° C. (347°–356° F.) to a thick liquid, which, on cooling, remains sticky, and only regains its original character after a long time.

Vulcanized rubber is india-rubber which has been caused to enter into combination with from 7 to 10 per cent. of sulphur by heating together the two substances to a temperature of 130°–150° C. (266°–302° F.). Vulcanized rubber differs from the natural article by possessing greater elasticity and flexibility, by resisting the action of solvents, reagents and atmosphere to a higher degree, and by not hardening when exposed to cold.

Hard rubber, vulcanite, or ebonite, is vulcanized rubber, containing from 20 to 35 per cent. of sulphur, and often also tar, white-lead, chalk, or other substances. It is hard, tough, and susceptible of a good polish.

Gutta-percha is the concrete juice of a tree—Isonandra gutta. It resembles india-rubber both in composition and properties. At ordinary temperature it is a yellowish or brownish, hard, somewhat flexible, but scarcely elastic substance; when warmed it softens, and is plastic above 60° C. (140° F.); at the temperature of boiling-water it is very soft. It is insoluble in water, alcohol, dilute acids and alkaline solutions; soluble in oil of turpentine, carbon disulphide and chloroform.

Stearoptens or Camphors are substances closely related to the terpenes and to cymene both in physical and chemical properties; while terpenes are liquids, camphors are crystalline solids. Borneo camphor has the composition $C_{10}H_{18}O$, while the camphor found in the camphor-trees of China and Japan has the composition $C_{10}H_{16}O$.

Camphor, Camphora, $C_{10}H_{16}O$ (*Laurinol*), forms white, translucent masses of a tough consistence and a crystalline structure; it has a characteristic, penetrating odor and poisonous properties; in the presence of a little alcohol or ether it may be pulverized; it is nearly insoluble in water, but soluble in alcohol, ether, chloroform, etc.; boiled with bromine it forms the *monobromated camphor*, $C_{10}H_{15}BrO$, of the U. S. P., a white crystalline substance having a mild camphoraceous odor and taste. Heating with nitric acid converts camphor into *camphoric acid*, $C_8H_{14}(CO_2H)_2$, a colorless, crystalline, fusible substance, having an acid taste; it is slightly soluble in water, readily in alcohol and ether.

Menthol, $C_{10}H_{19}OH$ (*Mint-camphor*). Found together with a terpene in oil of peppermint, and separates in crystals on cooling the oil. Menthol is nearly insoluble in water, fuses at 43° C. (109° F.) and boils at 212° C. (414° F.). It has the characteristic odor of peppermint.

Thymol, $C_{10}H_{14}O$ or $C_6H_3.CH_3.C_3H_7.OH$ (*Methyl-propylphenol*). Thymol is found in small quantities as a constituent of the volatile oils of wild thyme, horse-mint, and a few other plants.

Thymol crystallizes in large translucent plates, has a mild odor, a warm, pungent taste, melts at 50° C. (122° F.) and boils at 230° C. (446° F.) It is now largely used as an excellent and very valuable antiseptic, preference being given to it on account of its comparative harmlessness when compared with the strongly poisonous carbolic acid.

Thymol dissolved in moderately concentrated warm solution of potassium hydroxide, gives on the addition of a few drops of chloroform a violet color, which on heating soon changes into a beautiful violet-red.

Eucalyptol, $C_{10}H_{18}O$, is found in the volatile oils of different species of eucalyptus, as also in the oils of some other plants. It is liquid at the ordinary temperature, but solidifies when cooled to a little below the freezing-point. It has an aromatic, distinctly camphoraceous odor.

Benzoic acid, Acidum benzoicum, $HC_7H_5O_2$ or $C_6H_5CO_2H = 122$. Found in benzoin and some other resins; also in combination with other substances in the urine of herbivorous animals; it is obtained from benzoin by heating it carefully, when the volatile benzoic acid sublimes. It is now also manufactured from toluene, which is first converted into benzo-trichloride (trichlormethyl-benzene) by passing chlorine into hot toluene:

$$C_6H_5CH_3 + 6Cl = C_6H_5CCl_3 + 3HCl.$$

Benzo-trichloride, when treated with water under pressure, yields benzoic and hydrochloric acids, thus:

$$C_6H_5CCl_3 + 2H_2O = C_6H_5CO_2H + 3HCl.$$

Benzoic acid forms white, lustrous scales or friable needles, having a slight aromatic odor of benzoin, and an acid reaction; it is but slightly soluble in cold water, but easily soluble in alcohol, ether, oils, etc.

Benzoic acid, when neutralized with an alkali, gives a flesh-colored or reddish precipitate of ferric benzoate on the addition of a neutral solution of ferric chloride.

By neutralizing benzoic acid with either ammonium hydroxide, sodium hydroxide, or lithium carbonate, the official salts *ammonium benzoate*, $NH_4C_7H_5O_2$, *sodium benzoate*, $NaC_7H_5O_2.H_2O$, and *lithium benzoate*, $LiC_7H_5O_2$, are obtained. The three salts are white, soluble in water, and have a slight odor of benzoin.

Oil of bitter almond, Oleum amygdalæ amaræ, C_7H_6O or C_6H_5COH (*Benzaldehyde*). As shown by the formula, oil of bitter almond differs from benzoic acid in containing one atom less of oxygen; in all its reactions it behaves like a true aldehyde, being, for instance, easily converted into benzoic acid by oxidation.

It does not occur in a free state in nature, but is formed by a peculiar fermentation of a glucoside, *amygdalin*, existing in bitter almonds, in cherry-laurel, and in the kernels of peaches, cherries, etc., but not in sweet almonds. The ferment causing the decomposition of amygdalin is a substance termed *emulsine*, which is found in both bitter and sweet almonds. As water is required for the decomposition, the emulsine does not act upon the amygdalin contained in the same seed until water is added, when the decomposition takes place as follows:

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Glucose.}}{2C_6H_{12}O_6} + \underset{\text{Hydrocyanic acid.}}{HCN} + \underset{\text{Oil of bitter almond.}}{C_7H_6O.}$$

The oil is obtained by maceration of bitter almonds with water, and subsequent distillation when it distils over with hydrocyanic acid and steam, and separates as a heavy oil in the distillate.

It is an almost colorless, thin liquid of a characteristic aromatic odor, a bitter and burning taste, and a neutral reaction. The pure oil is not poisonous, but the crude oil of bitter almond is poisonous on account of its containing hydrocyanic acid.

Bitter almond water, Aqua amygdalæ amaræ, is made by dissolving 1 part of the oil in 999 parts of water.

Salicylic acid, Acidum salicylicum, $HC_7H_5O_3$ or $C_6H_4OH.CO_2H$ = 138. Derived from benzene by introducing one hydroxyl and one carboxyl radical. It is found in several species of violet, and in the form of methyl salicylate in the wintergreen oil (oil of Gaultheria procumbens). May be obtained by fusing potassium hydroxide with salicin.

Salicylic acid is manufactured from carbolic acid by passing carbon dioxide through sodium carbolate (sodium phenoxide), when sodium salicylate remains and carbolic acid distils over:

$$\underset{\text{Carbolic acid.}}{C_6H_5OH} + \underset{\text{Sodium hydroxide.}}{NaOH} = \underset{\text{Sodium carbolate.}}{C_6H_5ONa} + H_2O.$$

$$\underset{\text{Sodium carbolate.}}{2(C_6H_5ONa)} + \underset{\text{Carbon dioxide.}}{CO_2} = \underset{\text{Sodium salicylate.}}{C_6H_4NaOCO_2Na} + \underset{\text{Carbolic acid.}}{C_6H_5OH.}$$

Sodium salicylate, thus obtained, is decomposed by hydrochloric acid:

$$\underset{\text{Sodium salicylate.}}{C_6H_4ONaCO_2Na} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Salicylic acid.}}{C_6H_4OHCO_2H} + \underset{\text{Sodium chloride.}}{NaCl.}$$

Salicylic acid is a white, solid, odorless substance, having a sweetish, slightly acrid taste, and an acid reaction; it is but sparingly soluble in cold water, but readily soluble in alcohol, ether, etc.; it fuses at about 157° C. (315° F.), and sublimes at 200° C. (392° F.). It is a valuable antiseptic.

By dissolving the alkali hydroxides in salicylic acid, the various salts may be obtained, as, for instance, *sodium salicylate,* $NaC_7H_5O_3$, and *lithium salicylate,* $LiC_7H_5O_3$, both of which are white, soluble salts.

Analytical reactions.

1. Add to solution of salicylic acid or its salts ferric chloride: a reddish-violet color is produced, yet noticeable in solutions containing 1 part of salicylic acid in 500,000 parts of water. (Plate VI., 2.)

2. Add some cupric sulphate: a bright-green color will result.

3. Dissolve some salicylic acid or sodium salicylate in methyl alcohol and add one-fourth the volume of sulphuric acid. Heat

gently and set aside for a few minutes. On reheating, the odor of methyl salicylate is developed.

Salicin, $C_{13}H_{18}O_7$. This glucoside is found in several species of Salix (willow), and is mentioned here because it splits into glucose and salicylic alcohol, $C_6H_4.OH.CH_2OH$, when boiled with dilute acids:

$$C_{13}H_{18}O_7 + H_2O = C_6H_{12}O + C_7H_8O_2.$$

Salicylic alcohol is converted by chromic acid into salicylic aldehyde, C_6H_4 OH.COH, which by further oxidation is converted into salicylic acid.

Salicin forms white, silky, shining needles, which are soluble in less than an equal weight of water, have a neutral reaction and a very bitter taste.

Salicin sprinkled upon concentrated sulphuric acid produces a red color. Boiled with very dilute hydrochloric acid for a few minutes, and this solution nearly neutralized with sodium carbonate, a violet color is produced on the addition of a drop of ferric chloride solution.

Methyl salicylate, $CH_3.C_7H_5O_3$. Oil of wintergreen is chiefly methyl salicylate, a nearly colorless liquid with a characteristic, strongly aromatic odor. It is made by the method so extensively used in the manufacture of compound ethers, viz., by heating of salicylic acid with methyl alcohol in the presence of sulphuric acid. (See above reaction 3 of salicylic acid.)

Phenyl salicylate, Salol, $C_6H_5.C_7H_5O_3$. This compound ether is a white, crystalline, tasteless powder, which is nearly insoluble in water, readily soluble in alcohol, ether, and benzol, and fuses at 42° C. (107.4° F.). It is used as an antiseptic and antipyretic.

Salol heated with potassium hydroxide solution causes its decomposition into phenol, which can be recognized by its odor, and potassium salicylate, from which crystalline salicylic acid will separate upon supersaturating the liquid with hydrochloric acid. An excess of bromine-water produces a white precipitate in an alcoholic solution of salol.

Salol is made by the action of suitable dehydrating agents upon a mixture of phenol and salicylic acid:

$$C_6H_5OH + HC_7H_5O_3 = C_6H_5.C_7H_5O_3 + H_2O.$$

Phtalic acid, $C_6H_4.(CO_2H)_2$, is a dibasic acid, which, when heated, loses water, and is converted into phtalic anhydride:

$$C_6H_4.(CO_2H)_2 = H_2O + C_6H_4C_2O_3.$$

The latter compound, when treated with phenol in the presence of sulphuric acid, forms *phenol-phtalein:*

$$\underset{\text{Phenol.}}{2C_6H_6O} + \underset{\text{Phtalic anhydride.}}{C_8H_4O_3} = H_2O + \underset{\text{Phenol-phtalein.}}{C_{20}H_{14}O_4}.$$

A solution of phenol-phtalein shows a purplish-red color in the presence of alkalies; this color is destroyed by acids. This property is made use of in alkalimetry, where phenol-phtalein serves as an indicator.

Gallic acid, Acidum gallicum, $HC_7H_5O_5$, or $C_6H_2(OH)_3.CO_2H =$ 170. Obtained by exposing moistened nut-galls to the air for about six weeks, when a peculiar fermentation takes place, during which tannic acid is converted into gallic acid, which is purified by crystallization. The crystals contain one molecule of water, which may be expelled at 100° C. (212° F.). It is a white, solid substance, forming long, silky needles; it has an astringent and slightly acidulous taste, and an acid reaction; it is soluble in about 100 parts of cold or in 3 parts of boiling water, also readily soluble in alcohol, but sparingly in ether and chloroform; it gives a bluish-black precipitate with ferric salts, and does not coagulate albumin, nor precipitate alkaloids, gelatin, or starch. A piece of potassium cyanide added to solution of gallic acid produces a deep rose color.

Pyrogallol, Pyrogallic acid, $C_6H_3.(OH)_3$. When gallic acid is heated to 200° C. (392° F.) it is decomposed into carbon dioxide and pyrogallol, a substance which is not a true acid, but tri-hydroxy-benzene, *i. e.*, a tri-atomic phenol. Pyrogallol crystallizes in colorless needles, melts at 131° C. (268° F.), is easily soluble in water, ether, and alcohol. In alkaline solution it absorbs oxygen rapidly, assuming a red, then reddish-brown and dark-brown color (Plate VI., 3). Nitric acid also colors it yellow, then brown, and this property is made use of in testing for traces of nitric acid. Solutions of silver, gold, and mercury are reduced by pyrogallol even in the cold.

Tannic acid, Acidum tannicum, $HC_{14}H_9O_9 = 322$ (*Gallotannic acid*, *Digallic acid*). There are a number of tannic acids, or *tannins*, found in various parts of different plants (oak-bark, nut-galls, cinchona, coffee, tea, etc.), the properties of which are not quite identical. All tannins, however, are amorphous, have a faint acid reaction and strongly astringent properties; they all precipitate albumin and most of the alkaloids; they give with ferric salts a dark-colored solution or precipitate, the color being dark green or dark blue; they form with animal substances compounds which do not putrefy. Use is made of this property in the process of tanning—*i. e*, converting hides into leather.

The official or gallotannic acid is obtained by extracting nut-galls with ether and alcohol, and evaporating the solution; it forms light-yellowish, amorphous scales, having a faint and characteristic odor, a strongly astringent taste and an acid reaction; it is easily soluble in water and diluted alcohol.

Analytical reactions:

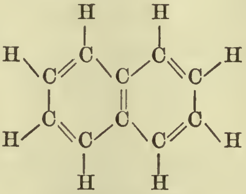
1. To solution of tannic acid add ferric chloride: a blue-black precipitate falls, soluble in large excess of tannic acid with violet color (Plate VI., 4). If ferric chloride is added in excess, the black precipitate dissolves in it with green color.

2. Add a few drops of potassium hydroxide: a brown coloration results.

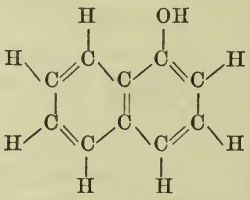
3. To a dilute solution (1 in 100) of tannic acid add gradually lime-water. A white precipitate falls, which on addition of more lime-water becomes blue by reflected, green by transmitted light, and darkens by exposure to air.

4. Tannic acid precipitates solutions of gelatin, albumin, gelatinized starch, tartar emetic, and most of the alkaloids.

Naphtalin, $C_{10}H_8$ (*Naphtalene*). The constitution of all benzene-derivatives considered so far, may be explained by the introduction of radicals in benzene. Naphtalin and its derivatives must be assumed to be formed by the union of two benzene residues in such a way that they have two carbon atoms in common, as represented in these formulas:



Naphtalin, $C_{10}H_8$.



Naphtol, $C_{10}H_7.OH$.

Naphtalin has been mentioned as a product of the destructive distillation of coal, and is obtained from that portion of coal-tar which boils between 180° and 220° C. (356° and 428° F.). This distillate is treated with caustic soda and then with sulphuric acid and distilled with water vapor.

When pure, naphtalin forms colorless, lustrous crystalline plates, having a penetrating but not unpleasant odor and a burning, aromatic taste. It fuses at 80° C. (176° F.), and boils at 218° C. (424° F.), but volatilizes slowly at ordinary temperature, and readily with water vapor. It is only sparingly soluble in water, but easily soluble in alcohol, ether, chloroform, etc. Impure naphtalin assumes, when exposed to light, a reddish or brownish color. Naphtalin is converted into phtalic acid by oxidizing agents.

Naphtol, $C_{10}H_7OH$. This compound bears to naphtalin the same relation as phenol to benzene—*i. e.*, hydroxyl replaces hydrogen in the respective hydrocarbons. Two isomeric naphtols are known, which differ in their physical properties and in their physiological action. The naphtol which is used medicinally is chiefly *beta-naphtol*, a solid compound crystallizing in thin, shining plates, having an odor similar to phenol and a burning, acrid taste. It fuses at 122° C. (252° F.), boils at 286° C. (547° F.), is insoluble in about 1000 parts of cold or 75 parts of boiling water; and readily soluble in alcohol, ether, chloroform, and fatty oils. The aqueous solution is colored green by ferric chloride. Naphtol is found in coal-tar, but is usually prepared from naphtalin.

Santonin, $C_{15}H_{18}O_3$. Although many efforts have been made to disclose the constitution of santonin, and though many derivatives of it have been formed, we know as yet but little of its structure, but it may be the anhydride of *santonic acid*, $C_{15}H_{20}O_4$. As several reactions point to a relationship between santonin and naphtalin, it is mentioned in this place.

Santonin is the active principle of wormseed, the unexpanded flowerheads of Artemisia, from which it is obtained by extraction with alcohol and lime-water, and decomposition of the soluble compound of lime and santonin by an acid. Santonin crystallizes in colorless prisms, which turn yellow on exposure to light; it is but sparingly soluble in water, more soluble in alcohol and ether.

Santonin taken internally confers upon the urine a dark color resembling the color of urine containing bile; upon heating such urine it turns cherry-red or crimson, the color disappearing on the addition of an acid, and reappearing on neutralization.

Analytical reactions:

1. Santonin added to alcoholic solution of potassium hydroxide produces a bright-red liquid which gradually becomes colorless. (Plate VI., 5.)

2. To 1 c.c. of sulphuric acid add a few drops of ferric chloride solution and a crystal of santonin: on heating, a dark-red color is produced, changing into violet-brown.

QUESTIONS.—471. What is the difference between fatty and aromatic compounds, and from which two hydrocarbons are they derived? 472. From what source is benzene obtained, how can it be made from benzoic acid, and what are its properties? 473. Give the graphic formulas of benzene, nitro-benzene, cymene, phenol, thymol, benzoic acid, and salicylic acid. Mention methane derivatives which have a constitution analogous to that of the substances mentioned. 474. Give composition, properties, and mode of manufacture of,

49. BENZENE DERIVATIVES CONTAINING NITROGEN.

Aniline, Phenyl-amine, $C_6H_5NH_2$. The constitution of amines, to which class aniline belongs, has been considered in Chapter 47. Aniline is found in coal-tar and in bone-oil; it is manufactured on a large scale by the action of nascent hydrogen upon nitro-benzene, iron and hydrochloric acid being generally used for generating the hydrogen.

Experiment 59. Dissolve 20 c.c. of nitro-benzene (this may be obtained according to the directions given in Experiment 57, using larger quantities of the material) in alcoholic ammonia and pass through this solution hydrogen sulphide as long as a precipitate of sulphur is produced; the reaction takes place thus:

$$C_6H_5NO_2 + 3H_2S = C_6H_5NH_2 + 2H_2O + 3S.$$

Evaporate on a water-bath to expel ammonium sulphide and alcohol; add to the residue dilute hydrochloric acid, which dissolves the aniline, but leaves any unchanged nitro-benzene undissolved. Separate the nitro-benzene from the aniline chloride solution, evaporate this to dryness, mix with some lime, in order to liberate the aniline, which may be obtained by distillation from a dry flask.

Pure aniline is a colorless, slightly alkaline liquid, having a peculiar, aromatic odor, a bitter taste, and strongly poisonous properties. It boils at 184.5° C. (364° F.). Like all true amines, it combines with acids to form well-defined salts.

Aniline dyes. The crude benzene used in the manufacture of aniline dyes is generally a mixture of benzene, C_6H_6, and toluene, C_7H_8. This mixture is first converted into nitro-benzene, $C_6H_5NO_2$, and nitro-toluene, $C_7H_7NO_2$, and then into aniline, $C_6H_5NH_2$, and toluidine, $C_7H_7NH_2$. When these substances are treated with oxidizing agents, such as arsenous and arsenic oxides, hypochlorites, chromic or nitric acid, etc., various substances are obtained which are either

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and tests for carbolic acid. 475. What substances are known as terpenes, where are they found in nature, and how are they related to camphors? 476. What relation exists between benzoic acid and oil of bitter almond? 477. What is the source of amygdalin, to which class of substances does it belong, and what are the products of its decomposition under the influence of emulsine? 478. Explain the process for the manufacture of salicylic acid from phenol, and state its properties. 479. Give composition and properties of naphtalin and naphtol. 480. Give tests for tannin, state the source from which it is derived, and for what it is used.

themselves distinguished by beautiful colors or may be converted into numerous derivatives showing all the various shades of red, blue, violet, green, etc.

As an instance of the formation of an aniline dye may be mentioned that of *rosaniline,* which takes place thus:

$$\underset{\text{Aniline.}}{C_6H_7N} + \underset{\text{Toluidine.}}{2C_7H_9N} + 3O = \underset{\text{Rosaniline.}}{C_{20}H_{19}N_3} + 3H_2O.$$

Experiment 60. To some of the aniline obtained by performing Experiment 59 add a little solution of bleaching powder: a beautiful purple color is obtained. Treat another portion with sulphuric acid to which an aqueous solution of potassium dichromate has been added: a blue color is produced. A third quantity treat with solution of cupric sulphate and potassium chlorate: a dark color is the result.

Diphenyl-amine, $(C_6H_5)_2NH$, is obtained by the destructive distillation of triphenyl-rosaniline (aniline blue) as a grayish crystalline substance, slightly soluble in water, more soluble in acids. A 0.2 per cent. solution in diluted sulphuric acid (forming diphenyl-sulphonic acid) is colored intensely blue by nitric acid; also, temporarily by nitrous acid and, somewhat less intensely, by hypochlorous, bromic, and iodic acids, and a number of other oxidizing agents.

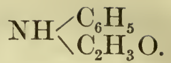
Meta-phenylene-diamine, or Diamido-benzol, $C_6H_4(NH_2)_2$, is obtained by the reduction of meta-dinitrophenol as a grayish crystalline powder. It has strongly basic properties, is somewhat soluble in water, readily soluble in alcohol or ether. It is a valuable reagent for nitrites, as it forms with even traces of nitrous acid an intense yellow color.

Sulphanilic acid, Aniline-para-sulphonic acid, $C_4H_6.NH_2.SO_3H$. Obtained by heating 1 part of pure aniline oil with 2 parts of fuming sulphuric acid, and purifying the product by crystallization.

$$C_6H_5.NH_2 + H_2SO_4 = C_6H_4.NH_2.SO_3H + H_2O.$$

It is a colorless crystalline substance, soluble in 182 parts of cold water. When sulphanilic acid is acted upon by nitrous acid, it is converted into *diazo-benzol-sulphonic acid,* $C_6H_5NNSO_4H$, which is of interest because it is used as a reagent in Ehrlich's diazo-reaction in urinary analysis.

Acetanilid, Antifebrine, C_8H_9NO or $C_6H_5.NH.C_2H_3O$ (*Phenyl-acetamide*). The term anilid is used for derivatives of aniline obtained from this compound by replacement of the ammonia hydrogen (or amido hydrogen) by radicals, and according to the introduction of an alcohol radical or acid radical a distinction is made between "alcohol anilids" and "acid anilids."

If the radical used for replacing the hydrogen in aniline is acetyl, C_2H_3O, the radical of acetic acid, the resulting compound is acetanilid, the constitution of which is represented in the formula  $NH\begin{cases}C_6H_5\\C_2H_3O\end{cases}$. It is obtained by boiling together for one or two days equal weights of pure aniline and glacial acetic acid, distilling and collecting the portion which passes over at a temperature of about 295° C. (563° F.). The distillate solidifies on cooling and may be purified by recrystallization from solution in water. The chemical change taking place is this:

$$C_6H_5NH_2 + C_2H_4O_2 = C_6H_5.NH.C_2H_3O + H_2O.$$

Pure acetanilid forms white, odorless crystals of a silken lustre and a greasy feeling to the touch. It fuses at 113° C. (235° F.) and boils at 295° C. (563° F.); it is but slightly soluble in cold, much more soluble in hot water, readily soluble in alcohol and ether; the solutions have a neutral reaction and are not colored by either concentrated sulphuric acid or by ferric chloride.

Analytical reactions:

1. When 0.1 gramme acetanilid is boiled with 1 c.c. hydrochloric acid and to this solution is added 1 c.c. each of saturated solutions of carbolic acid and of bleaching powder, a turbid red liquid is obtained which turns dark-blue when supersaturated with ammonia water. (Plate VI., 6.)

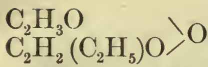
2. On heating 0.1 gramme of acetanilid with a few c.c. of concentrated solution (1 in 4) of potassium hydroxide, the odor of aniline becomes noticeable; on now adding chloroform, and again heating, the disagreeable odor of the poisonous phenyl-isonitril, C_6H_5NC, is evolved.

3. A mixture of equal parts of acetanilid and sodium nitrite sprinkled upon concentrated sulphuric acid produces a bright-red color.

Phenyl-hydrazine, $C_6H_5.NH.NH_2$. Hydrazine compounds are substances derived from the hypothetical body N_2H_4 (or $NH_2—NH_2$) by replacement of hydrogen atoms by alcohol radicals. They possess strong basic properties and unite directly with acids, like amines or amides. Phenyl-hydrazine is of interest because it is used in the manufacture of antipyrine, and also because it is a valuable reagent for the detection of aldehydes and sugars.

It is obtained by treating aniline chloride first with sodium nitrite, and then with nascent hydrogen. It is an oily liquid forming white crystals at a low temperature; it is sparingly soluble in water, but readily in hydrochloric acid, with which it combines to form the hydrochloride

Antipyrine, $C_{11}H_{12}N_2O$ or $C_9H_6NO(CH_3)_2N_2O$ (*Phenyl-dimethyl-pyrazolon*). When phenyl-hydrazine is heated with *diacetic ether*,


$\left.\begin{matrix}C_2H_3O\\C_2H_2(C_2H_5)O\end{matrix}\right\rangle O$, a substance is formed known as phenyl-methyl-pyrazolon, $C_{10}H_{10}N_2O$.

In this compound a second hydrogen atom may be replaced by methyl, when phenyl-dimethyl-pyrazolon is formed, which is the substance to which the name antipyrine has been given.

Antipyrine is a white, crystalline, odorless powder, having a slightly bitter taste; it fuses at 113° C. (235° F.), is soluble in less than its own weight of water, in one part of alcohol, in one part of chloroform, but only in 50 parts of ether.

Analytical reactions:

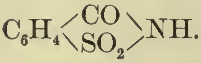
1. 0.2 gramme of antipyrine dissolve in 2 c.c. of nitric acid without change of color. On heating slightly the liquid assumes a yellow, then an intense red color. (Plate VI., 7.)

2. 2 c.c. of a 5 per cent. solution of antipyrine treated with a few drops of potassium nitrite solution yield an intense green color on the addition of ten drops of acetic acid. (Plate VI., 8.) In a more concentrated solution green crystals of nitroso-antipyrine form on standing.

3. The addition of ferric chloride to solution of antipyrine causes a deep red color.

4. Mercuric chloride, as well as tannic acid, produces a white precipitate.

Saccharine, $C_7H_5SO_3N$ or $C_6H_4.CO.SO_2NH$ (*Benzoic sulphinide, Anhydro ortho-sulphamine-benzoic acid*). This substance is a derivative of benzoic acid, $C_6H_5.CO_2H$, obtained from it by introducing the two bivalent radicals SO_2 and NH with elimination of water. The constitution is, therefore, represented by the formula


$C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle NH.$

Practically, saccharine is not made from benzoic acid, but from toluol, $C_6H_5.CH_3$, by a series of rather complicated synthetical processes.

Saccharine is a white, amorphous or somewhat crystalline powder, having a very slight odor of oil of bitter almond, which becomes more perceptible on heating the substance. It is but sparingly soluble in water, requiring about 400 parts for solution; this solution is slightly acid and has an extremely sweet taste, which is yet perceptible when saccharine is dissolved in 70,000 parts of water, which shows that it is about 280 times sweeter than cane-sugar, a solution of which in 250 parts of water is yet perceptibly sweet. Saccharine is soluble in alcohol and ether, and it is this latter property which is made use of in testing sugar (or other substances insoluble in ether) for saccharine. The substances are treated with ether, which is filtered off and evaporated, when the saccharine may be recognized by its taste in the remaining residue.

Pyrrole, C_4H_5N. During the destructive distillation of certain nitrogenous matters (chiefly bones), a liquid known as *bone-oil* is obtained, which contains a number of nitrogenous basic substances, among which pyridine and pyrrole are found. Pyrrole has but weak basic properties, is insoluble in water and has an odor like chloroform.

A solution of pyrrole in alcohol, treated with iodine in the presence of oxidizing agents, such as ferric chloride, deposits after some time crystals of *tetra-iodo pyrrole*, C_4HI_4N. This compound is used under the name of *iodol.* It is a pale-yellow, crystalline powder, almost insoluble in water, soluble in 3 parts of alcohol, 1 part of ether, and 15 parts of fatty oils; it is, when pure, tasteless and odorless, and contains of iodine 88.97 per cent.

Pyridine, C_5H_5N. This substance has been mentioned above as being a constituent of bone-oil. Other substances have been isolated from this oil and have been found to form a homologous series:

Pyridine, C_5H_5N
Picoline, C_6H_7N
Lutidine, C_7H_9N
Collidine, $C_8H_{11}N$

Pyridine is of special interest, because it has been found that several of the alkaloids, such as quinine, cinchonine, etc., when oxidized, yield acids containing nitrogen, which bear to pyridine the same relation that benzoic acid bears to benzene, or that acetic acid bears to methane.

Thus, when nicotine is treated with oxidizing agents, nicotinic acid, $C_6H_5NO_2$, is obtained, which, when distilled with lime, breaks up into pyridine and carbon dioxide, thus:

$$C_6H_5NO_2 = C_5H_5N + CO_2.$$

The relation of nicotinic acid to pyridine, of benzoic acid to benzene, acetic acid to methane, may be shown thus:

$CH_3.H$ Methane.	$C_6H_5.H$ Benzene.	$C_5H_4N.H$ Pyridine.
$CH_3.CO_2H$ Acetic acid.	$C_6H_5.CO_2H$ Benzoic acid.	$C_5H_4N.CO_2H.$ Nicotinic acid.

Pyridine is also obtained together with another basic substance, termed quinoline, C_9H_7N, by distilling quinine or cinchonine with potash. These observations, showing an intimate relationship between alkaloids and the pyridine and quinoline bases, have led to numerous experiments made with the view of either solving the problem of making alkaloids synthetically, or of obtaining substances which might have physiological actions similar to those of the alkaloids. The result of these efforts has been the introduction into the materia medica of quite a number of new remedies.

Pyridine is a colorless liquid, having a sharp, characteristic odor, strongly basic properties, and a boiling-point of 116° C. (241° F.).

Quinoline, C_9H_7N (*Chinoline*), has been mentioned above as a product of the distillation of quinine with potash; it may also be obtained by the action of sulphuric acid upon a mixture of aniline, nitro-benzene, and glycerin. It is, like pyridine, a colorless liquid, but its aromatic odor is less pleasant and its basic properties are less marked than those of pyridine. Boiling-point 237° C. (458° F.).

Kairine, $C_{10}H_{13}.NO.HCl$. The name kairine has been given to the hydrochloride of methyl-oxychinoline hydride. It is a white, crystalline, odorless powder, soluble in 6 parts of water or in 20 parts of alcohol.

Thalline, $C_{10}H_{11}NO$ (*Tetra-hydro-paramethyl-oxyquinoline*). Quinoline serves in the manufacture of thalline, a white, crystalline substance, which has an aromatic odor, fuses at 40° C. (104° F.) and is soluble in water, alcohol, and ether. The most characteristic feature of the substance is that it is colored intensely green by various oxidizing agents, such as ferric chloride and others. Some of the salts of thalline, chiefly the sulphate, tartrate, and tannate, have been used medicinally.

50. ALKALOIDS.

General Remarks. The basic substances found in plants are grouped together under the name of alkaloids, this term signifying alkali-like, in allusion to the alkaline or basic properties of these substances. They belong either to the amines (compounds containing carbon, hydrogen, and nitrogen only), or to the amides (com-

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QUESTIONS.—481. From what, and by what process is aniline obtained; what is its composition and what its constitution? 482. How are aniline dyes manufactured from aniline? 483. What is the difference between an amide and an anilid? 484. What is the composition of antifebrine, and how is it made? 485. State the properties and some reactions characteristic of antipyrine. 486. What is saccharine, and what are its properties? 487. Mention some constituents of bone-oil. 488. State the composition of iodol. 489. Explain the relation existing between methane, benzene, pyridine, and the compounds obtained from these three bodies by introducing carboxyl. 490. Mention two processes by which, and two sources from which pyridine may be obtained.

pounds containing, besides the three elements named, also oxygen), and show their derivation from ammonia to a more or less marked degree, as, for instance, in their power to combine with acids without elimination of water, to combine with platinic chloride to form insoluble double compounds, etc.

The compounds formed by the direct combination of alkaloids with acids are, in the case of oxygen acids, named like other salts of these acids, for instance, sulphates, nitrates, acetates, etc. In the case of halogen acids, however, a different method has been adopted, because it would be incorrect to apply the terms chlorides and bromides to substances formed not by the combination of chlorine or bromine with other substances, nor by the replacement of hydrogen in the respective hydrogen acids of these elements, but by direct combination of these acids with the alkaloids. The terms *hydrochloride* and *hydrobromide* would have been very appropriate, but the terms *hydrochlorate* and *hydrobromate* have been adopted by the U. S. P. for the compounds obtained by direct union of alkaloids with hydrochloric and hydrobromic acids.

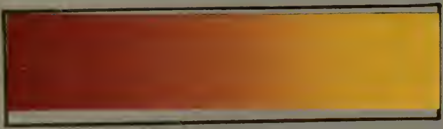
Alkaloids are found in the leaves, stems, roots, barks, and seeds of various plants; it often happens that a certain alkaloid is found in the different species of one family, and it is also often the case that various alkaloids of a similar composition are found in the same plant.

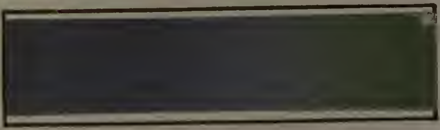
General properties of alkaloids:

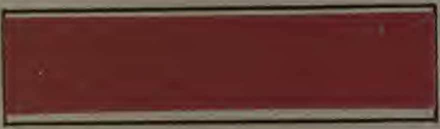
1. They combine with acids (without elimination of water) to form well-defined salts, and are set free from the solutions of these salts by alkalies and alkali carbonates.
2. Those containing no oxygen (amines) are, in most cases, volatile liquids, those containing oxygen (amides), are non-volatile solids.
3. The volatile alkaloids have a peculiar, disagreeable odor reminding of ammonia; the non-volatile alkaloids are odorless.
4. Most solid alkaloids fuse at a temperature above 100° C. (212° F.) without decomposition, but are decomposed when the heat is raised much beyond the fusing-point.
5. Most alkaloids are insoluble, or nearly so, in water, but soluble in alcohol, chloroform, benzene, acetic ether, and many also in ether.
6. The chlorides, sulphates, nitrates, acetates (and most other salts) of alkaloids are either soluble in water, or in water which has been slightly acidulated, and also in alcohol; but they are insoluble, or nearly so, in ether, acetic ether, chloroform (except veratrine and

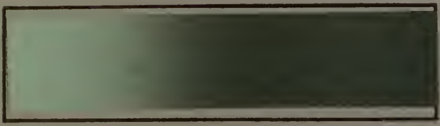
PLATE VII.

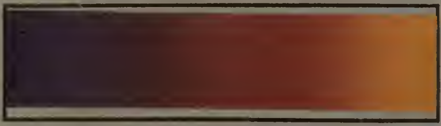
ALKALOIDS.

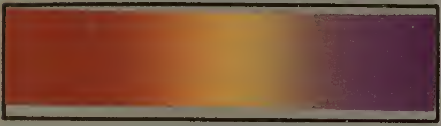
1

Morphine treated with nitric acid.

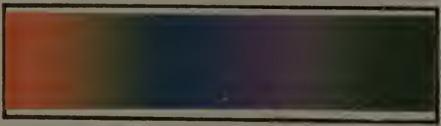
2

Morphine treated with solution of ferric chloride.

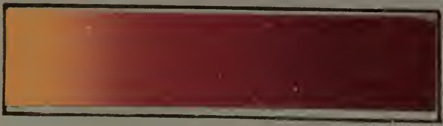
3

Codeine treated with bromine water and ammonia water.

4

Quinine treated with chlorine water and ammonia water.

5

Strychnine treated with sulphuric acid and potassium dichromate.

6

Brucine treated with nitric acid and with sodium thiosulphate.

7

Physostigmine treated successively with ammonia water, alcohol, acetic acid, and again with ammonia water.

8

Veratrine treated with sulphuric acid.

narcotine), amyl alcohol (except veratrine and quinine), benzene, and benzin.

7. The solid alkaloids, as well as their salts, may be obtained in a crystalline state.

8. Most alkaloids are white.

9. Most alkaloids have a very strong, generally bitter taste.

10. Most alkaloids act very energetically upon the animal system.

11. From the aqueous solutions of alkaloid salts, the solid alkaloids are precipitated by alkali hydroxides, in an excess of which reagents some alkaloids (morphine, for instance) are soluble. Alkali carbonates and bicarbonates liberate all, and precipitate most alkaloids; not precipitated by bicarbonates are strychnine, brucine, veratrine, atropine, and a few rare alkaloids.

Most alkaloids give precipitates with tannic acid, picric acid, phospho-molybdic acid, potassium mercuric iodide; and the higher chlorides of platinum, gold, and mercury.

12. Most alkaloids give beautiful color reactions when treated with oxidizing agents, such as nitric acid, chloric acid, chromic acid, ferric chloride, chlorine water, etc.

A decinormal solution of mercuric-potassium iodide, $HgI_2.(KI)_2$, made by dissolving 13.546 grammes mercuric chloride and 49.8 grammes potassium iodide in 1000 c.c of water, is known as *Mayer's solution.* This precipitates all alkaloids, forming with them white or yellowish-white, generally crystalline compounds of definite composition, for which reason this solution is used for volumetric determination of alkaloids. (In most cases the alkaloid replaces the potassium in the potassium-mercuric iodide.)

Phospho-molybdic acid, mentioned above as a reagent for alkaloids, is prepared as follows: 15 grammes ammonium molybdate are dissolved in a little ammonia water and diluted with water to 100 c.c. This solution is poured gradually into 100 c.c. of nitric acid, specific gravity 1.185, and to this mixture is added a warm 6 per cent. solution of sodium phosphate as long as a precipitate is produced. This precipitate is collected on a filter, washed and dissolved in very little sodium hydroxide solution; the solution is evaporated to dryness, further heated until all ammonia has been expelled and the residue dissolved in 10 parts of water. To this solution is added a quantity of nitric acid sufficient to redissolve the precipitate which is formed at first. This reagent gives precipitates not only with the alkaloids, but also with the salts of potassium and ammonium.

General mode of obtaining alkaloids. The disintegrated vegetable substance (bark, seeds, etc.) is extracted with acidified water, which dissolves the alkaloids. When the alkaloid is volatile, it is obtained from this solution by distillation, after having been liberated by an alkali.

Non volatile alkaloids are precipitated from the acid solution by the addition of an alkali, and the impure alkaloid thus obtained is purified by again dissolving in an acid and reprecipitating, or by dissolving in alcohol and evaporating the solution.

As the quantity of alkaloids in plants, and consequently in the aqueous extract made from them, is often so small that the precipitation process gives unsatisfactory results, a second method known as the *shaking-out process* is often employed for the separation of alkaloids. In using this process the concentrated aqueous extract, to which a suitable alkaline precipitant has been added, is agitated with a liquid (such as chloroform) not miscible with water and acting as a solvent upon the alkaloids. The operation is performed in an apparatus known as *separator* or *separatory funnel*, consisting of a globular or cylindrical glass vessel, provided with a well-fitting stopper and an outlet-tube containing a glass stopcock. Having introduced into this vessel the extract and solvent, the latter is made to dissolve the alkaloids present by a rapid rotation of the separator. As the aqueous solution and the solvent do not mix, but form two distinct layers one above the other, they may be conveniently separated by opening the stopcock until the heavier liquid has run out. By evaporation of the liquid, used as a solvent, the alkaloids may be obtained in a more or less pure condition.

Antidotes. In cases of poisoning by alkaloids the stomach-pump and emetics (zinc sulphate) should be applied as soon as possible; astringent liquids may be given, because tannic acid forms insoluble compounds with most of the alkaloids. In some cases special physiological antidotes are known, and should be used.

Detection of alkaloids in cases of poisoning. The separation and detection of poisonous alkaloids in organic matter (food, contents of stomach, etc.), especially when present in very small quantities, as is generally the case, is one of the most difficult tasks of the toxicologist, and none but an expert who has made himself thoroughly familiar with the methods of discovering minute quantities of organic poisons in the animal system should undertake to make such an analysis in case legal proceedings depend on the result of the chemist's report.

Of the various methods applied for the separation of alkaloids from organic matter, the following may be mentioned:

The substance to be examined is properly comminuted (if this be necessary) and repeatedly digested at 40° to 50° C. (104° to 122° F.) with water slightly acidulated with sulphuric acid. The filtered liquids (containing the sulphates of the alkaloids) are evaporated over a water-bath to a thin syrup, which is mixed with three or four times its own volume of alcohol; this mixture is digested at about 35° C. (95° F.) for several hours, cooled, filtered, and again evaporated nearly to dryness. (By this treatment with alcohol many substances soluble in the acidified water, but insoluble in diluted alcohol, are eliminated and left on the filter, whilst the alkaloids remain in solution as sulphates.)

A little water is now added to the residue, and this solution, which should yet have a slight acid reaction, is shaken with about three times its own volume of acetic ether, which dissolves some coloring and extractive matters, but does not act upon the alkaloid salts. The two strata of liquids which form on standing in a tube are separated by means of a pipette, and the operation is repeated, if necessary, *i. e.*, if the ether should have been strongly colored.

The remaining acid aqueous solution is next slightly supersaturated with sodium carbonate, which liberates the alkaloids. Upon now shaking the solution with acetic ether, all alkaloids are dissolved in this liquid, which, after being separated from the aqueous solution, leaves upon evaporation, at a low temperature, the alkaloids generally in a sufficiently pure state for recognition by special tests. It may, however, be necessary to purify the residue further by neutralizing with an acid, allowing to crystallize in a watch-glass, and separating the small crystals from adhering mother-liquor.

The above method for detecting alkaloids in the presence of organic matter generally answers the requirements of students.

The practical toxicologist has in most cases of poisoning some data (deduced from the symptoms before death, or from the results of the post-mortem examination) pointing to a certain poison, which, of course, facilitate his work considerably.

Important alkaloids.

a. Liquid and volatile alkaloids.

Sparteine,	$C_{15}H_{26}N_2$	Scoparius.
Coniine,	$C_8 H_{17}N$	Conium maculatum.
Nicotine,	$C_{10}H_{14}N_2$	Tobacco plant.

b. Solid and fixed alkaloids.

Morphine,	$C_{17}H_{19}NO_3$	10.00 per cent.	In opium. The percentages given are an average, but vary widely.
Codeine,	$C_{18}H_{21}NO_3$	0.25 "	
Thebaine,	$C_{19}H_{21}NO_3$	0.15 "	
Papaverine,	$C_{21}H_{21}NO_4$	1.00 "	
Narcotine,	$C_{22}H_{23}NO_7$	1.30 "	
Narceine,	$C_{23}H_{29}NO_9$	0.70 "	
Pseudo-morphine,	$C_{17}H_{19}NO_4$	less than 0.1 per cent.	
Protopine,	$C_{20}H_{19}NO_5$		
Codamine,	$C_{20}H_{23}NO_4$		
Laudamine,	$C_{21}H_{27}NO_4$		
Meconidine,	$C_{21}H_{23}NO_4$		
Cryptopine,	$C_{21}H_{23}NO_5$		
Laudanosine,	$C_{21}H_{27}NO_4$		
Quinine,	$C_{20}H_{24}N_2O_2 + 3H_2O$		In cinchona bark.
Cinchonine,	$C_{19}H_{22}N_2O$		
Quinidine,	isomere to quinine		
Cinchonidine,	isomere to cinchonine		
Strychnine,	$C_{21}H_{22}N_2O_2$		In nux vomica.
Brucine,	$C_{23}H_{26}N_2O_4 + (4H_2O)$		
Atropine,	$C_{17}H_{23}NO_3$		In solanaceæ.
Hyoscyamine,	$C_{17}H_{23}NO_3$		
Hyoscine,	$C_{17}H_{21}NO_4$		

Cocaine,	$C_{17}H_{21}NO_4$	Erythroxylon coca.
Veratrine,	?	Asagræa officinalis.
Aconitine,	$C_{33}H_{45}NO_{12}$	Aconitum napellus.
Colchicine,	$C_{22}H_{25}NO_6$	Colchicum autumnale.
Berberine,	$C_{20}H_{17}NO_4$	Berberis vulgaris.
Hydrastine,	$C_{21}H_{21}NO_6$	Hydrastis canadensis.
Hydrastinine,	$C_{11}H_{11}NO_2$	
Physostigmine,	$C_{15}H_{21}N_3O_2$	Calabar bean.
Pilocarpine,	$C_{11}H_{16}N_2O_2$	Pilocarpus.
Caffeine,	$C_8H_{10}N_4O_2 + H_2O$	Coffee, tea.
Theobromine,	$C_7H_8N_4O_2$	Seeds of theobroma cacao.

Sparteine, $C_{15}H_{26}N_2$. This alkaloid, found in scoparius (broom, Irish broom), is a colorless, oily liquid, turning brown on exposure to air and light. It has a slight aniline-like odor.

Sparteine sulphate, $C_{15}H_{26}N_2H_2SO_4 + 4H_2O$, is obtained by saturating the alkaloid with sulphuric acid; it is a colorless, crystalline salt, readily soluble in water. An ethereal solution of the salt, to which a few drops of ammonia water have been added, deposits on the addition of an ethereal solution of iodine, minute dark greenish-brown crystals.

Coniine, $C_8H_{17}N$, occurs in conium maculatum (hemlock), accompanied by two other alkaloids. It is a colorless, oily liquid, having a disagreeable, penetrating odor.

Nicotine, $C_{10}H_{14}N_2$. Tobacco leaves contain from 2 to 8 per cent. of nicotine, which is a colorless, oily liquid, having a caustic taste and a disagreeable, penetrating odor. It gives with hydrochloric acid a violet, with nitric acid an orange color.

Opium is the concrete, milky exudation obtained, in the Orient, by incising the unripe capsules of papaver somniferum, poppy. Chemically, opium is a mixture of a large number of substances, containing besides glucose, fat, gum, albumin, wax, volatile and coloring matter, meconic acid, etc., not less than sixteen or eighteen different alkaloids, many of which are, however, present in minute quantities.

Ordinary opium should contain not less than 9 per cent., and when dried at 85° C. (185° F.) from 13 to 15 per cent. of morphine.

Dried and powdered opium, after having been exhausted with about ten times its weight of stronger ether (which dissolves chiefly the narcotine, but not the morphine salts), the ethereal solution filtered off, and the weight of the opium restored by sugar of milk, forms the *deodorized opium* of the U. S. P.

Experiment 61. Determine quantitatively the amount of morphine in a sample of opium by using the U. S. P. method, which is as follows: Introduce 10 grammes of opium (which, if fresh, should be in very small pieces, and if dry, in very fine powder) into a bottle having a capacity of about 300 c.c., add 100 c.c. of water, cork it well, and agitate it frequently during twelve hours. Then pour the whole as evenly as possible upon a wetted filter having a diameter of 12 centimeters, and, when the liquid has drained off, wash the residue with water until 150 c.c. of filtrate are obtained. Then transfer the moist opium back to the bottle, add 50 c.c. of water, agitate repeatedly during fifteen minutes, and return the whole to the filter. Wash the residue with water until the filtrate, to be collected in a second flask, measures 150 c.c.: finally, collect 20 c.c. more of a third filtrate. Next evaporate in a tared capsule, first, the second filtrate to a small volume, then add the first filtrate, rinsing the vessel with the third filtrate, and continue the evaporation until the residue weighs 14 grammes. Transfer this residue to a tared 100 c.c. flask and rinse the capsule with a few drops of water at a time, until the entire solution weighs 20 grammes. Then add 12.2 c.c. of alcohol, shake well, add 25 c.c. of ether, and shake again. Now add 3.5 c.c. of ammonia water from a pipette, stopper the flask, shake it thoroughly during ten minutes, and then set it aside for at least six hours.

Place in a funnel two rapidly-acting filters, of a diameter of 7 centimeters, one within the other, wet them with ether, and decant the ethereal solution upon the filter. Add 10 c.c. of ether to the contents of the flask, rotate it, and again decant the ethereal layer upon the filter. Repeat this operation with another portion of 10 c.c. of ether. Then pour into the filter the contents of the flask in such a way as to transfer the greater portion of the crystals to the filter, accomplishing this finally by washing the flask with several portions of water, using not more than 10 c.c. in all. Allow the filter to drain, then apply water to the crystals, drop by drop, until they are practically free from mother-water, and afterward wash them, drop by drop, from a pipette, with alcohol previously saturated with powdered morphine. When this has passed through, displace the remaining alcohol by ether, using about 10 c.c. Allow the filter to dry at a temperature not exceeding 60° C. (140° F.) until its weight remains constant, then transfer the crystals to a tared watch-glass and weigh them. The weight found, multiplied by 10, represents the percentage of crystallized morphine obtained from the specimen examined.

The explanation of the above process is as follows: By extracting opium with water a liquid is obtained containing in solution the total quantity of opium alkaloids, in the form of salts, alongside of numerous other substances. As it is desirable to work analytically with small volumes of liquids (in order to avoid loss through solubility of the precipitate), the aqueous solutions are evaporated to a small bulk. The addition of ammonia water causes the decomposition of the alkaloidal salts with precipitation of morphine, while certain other alkaloids, especially narcotine, remain dissolved in the ether which for this purpose has been added previously.

Morphine, Morphina, $C_{17}H_{19}NO_3.H_2O = 303$ (*Morphia*). A white crystalline powder, or colorless, shining, prismatic crystals, odorless, of a bitter taste, and an alkaline reaction to litmus; almost insoluble in ether and chloroform, very slightly soluble in cold water, soluble in 300 parts of cold and 36 parts of boiling alcohol; heated for some time at 100° C. (212° F.) it becomes anhydrous; at 254° C. (489° F.) it melts, forming a black liquid; heated with excess of hydrochloric acid for some hours, under pressure, to 150° C. (302° F.), it loses water, and is converted into *apomorphine*, $C_{17}H_{17}NO_2$, a crystalline, solid alkaloid, valuable as an emetic. *Apomorphine hydrochlorate*, $C_{17}H_{17}NO_2.HCl$, is official; it is a white salt, which turns green when exposed to the air, especially in the presence of moisture.

The above-mentioned process for the quantitative estimation of morphine in opium may be used for its manufacture; the crude morphine thus obtained is purified by crystallization.

Morphine combines with acids, and of the salts are official:

Morphine acetate,	Morphinæ acetas,	$C_{17}H_{19}NO_3.C_2H_4O_2.3H_2O$.
Morphine hydrochlorate,	Morphinæ hydrochloras,	$C_{17}H_{19}NO_3.HCl.3H_2O$.
Morphine sulphate,	Morphinæ sulphas,	$(C_{17}H_{19}NO_3)_2H_2SO_4.5H_2O$.

The above three salts are white, and soluble in water.

Analytical reactions:

1. Morphine or a morphine salt sprinkled upon nitric acid assumes an orange-red color, and then produces a reddish solution, gradually changing to yellow. (Plate VII., 1.)

2. Neutral solution of ferric chloride causes a blue color with morphine or with neutral solutions of morphine salts; the color is changed to green by an excess of the reagent, and is destroyed by free acids or alcohol, but not by alkalies. (Plate VII., 2.)

3. A fragment of iodic acid added to a strong solution of a morphine salt is decomposed, with liberation of iodine, which imparts a violet color to chloroform upon shaking the latter with the mixture.

4. A mixture of 2 parts of morphine and 1 part of cane-sugar added to concentrated sulphuric acid gives a rose-red color.

5. Morphine dissolves in cold, concentrated sulphuric acid, forming a colorless solution, which, after standing for several hours, turns pink or red on the addition of a trace of nitric acid.

6. Aqueous or acid solutions of morphine salts are precipitated by alkaline hydroxides; the precipitated morphine is soluble in potassium or sodium hydroxide, but not in ammonium hydroxide.

7. Neutral solutions of morphine afford yellow precipitates with the chloride of gold or platinum, with potassium chromate or dichromate, and with picric acid, but not with mercuric chloride.

Codeine, Codeina, $C_{18}H_{21}NO_3.H_2O = 317$. A white, crystalline powder, sparingly soluble in cold water, easily soluble in alcohol and chloroform. It is neutral to litmus, and has a faintly bitter taste.

Analytical reactions:

1. On adding to 5 c.c. of an aqueous solution of codeine (1 in 100) 10 drops of bromine water, shaking so as to redissolve the precipitate formed, and adding after a few minutes some ammonia water, the liquid assumes a claret-red tint. (Plate VII., 3.)

2. Codeine, dissolved in sulphuric acid containing 1 per cent. of sodium molybdate, forms at first a dirty-green solution, which after a while becomes pure blue, and gradually fades within a few hours to pale yellow.

3. Codeine, dissolved in sulphuric acid, forms a colorless liquid, which, upon being warmed with a trace of ferric chloride, becomes deep blue.

4. Crystals of codeine sprinkled upon nitric acid assume a red color, but the acid will acquire only a yellow, not a red color. (Difference from morphine.)

Narcotine, $C_{22}H_{23}NO_7$, and **Narceine,** $C_{23}H_{29}NO_9.2H_2O$, are white, crystalline opium alkaloids, which are almost insoluble in water, soluble in alcohol. Concentrated sulphuric acid forms with narcotine a solution which is at first colorless, but turns yellow in a few minutes, and purple on heating. Narceine dissolves in concentrated sulphuric acid with a gray-brown color, which changes to red when heated.

Meconic acid, $C_7H_4O_7.3H_2O$. A tribasic acid, characteristic of opium, in which it exists to the extent of 3 or 4 per cent., most likely combined with the alkaloids. It is a white, crystalline substance, soluble in water and alcohol.

Meconic acid forms with ferric chloride a blood-red color, which is not affected by dilute acids or by mercuric chloride (different from ferric sulphocyanate), but disappears on the addition of stannous chloride and of the alkali hypochlorites. This test may be used in cases of poisoning to decide whether opium or morphine is present.

Cinchona alkaloids. The bark of various species of cinchona contains a number of alkaloids, of which the most important are quinine, cinchonine, quinidine, and cinchonidine. These alkaloids exist in the bark in combination with a peculiar acid, termed *kinic acid.* The quantity and relative proportion of the alkaloids vary widely in different barks, but the official bark should contain not less than 5 per cent. of total alkaloids, and at least 2.5 per cent. of quinine.

Determination of the total alkaloids and of quinine in Cinchona. The U. S. P. has adopted the following method for the assay of cinchona:

1. *For total alkaloids.* To 20 grammes of finely-powdered cinchona, and contained in a glass-stoppered flask, add 200 c.c. of a previously prepared mixture of 19 volumes of alcohol, 5 volumes of chloroform, and 1 volume of ammonia water; shake the mixture frequently during four hours. Then filter into a bottle through a funnel containing a pellet of cotton, in such a manner that no material loss by evaporation may result. Transfer 100 c.c. of the filtrate to a beaker and evaporate to dryness. Dissolve the residue of crude alkaloids thus obtained in 10 c.c. of water and 4 c.c. of normal sulphuric acid; with the aid of a gentle heat, filter the cooled solution into a separatory funnel, and wash the beaker and filter until the filtrate no longer has an acid reaction, using as small a quantity of water as possible. Now add 5 c.c. of normal potassium hydrate, or such an amount as will render the liquid decidedly alkaline, and extract the alkaloids by shaking the mixture, first with 20 c.c., and then repeatedly with 10 c.c. of chloroform, until a drop of the last chloroform extraction, when evaporated on a watch-glass, no longer leaves a residue. Evaporate the chloroformic extracts in a tared beaker, dry the residue at 100° C. (212° F.), and weigh. The weight found, multiplied by 10, will give the percentage of total alkaloids.

2. *For quinine.* Transfer 50 c.c. of the clear filtrate remaining over from the preceding process to a beaker, evaporate it to dryness, and proceed as directed in the assay for total alkaloids, using, however, only one-half the amounts of volumetric acid and alkali there directed Add the united chloroformic extracts gradually, and in small portions at a time, to about 5 grammes of powdered glass contained in a porcelain capsule placed over a water-bath. After the chloroform has been expelled moisten the residue with ether, and, having placed a funnel containing a filter of a diameter of 7 centimeters, and well wetted with ether, over a small graduated tube (A), transfer to the filter the ether-moistened residue from the capsule. Rinse the latter several times with fresh ether, so as to transfer the whole of the residue to the filter, then percolate with ether, drop by drop, until 10 c.c. of percolate have been obtained. Then collect another percolate of 10 c.c. by similar slow percolation with ether, in a second graduated tube (B). Transfer the contents of the two tubes completely (using ether for washing) to two small, tared capsules (marked A and B), evaporate at 100° C. (212° F.) and weigh them. From the weight of residue obtained in A deduct that contained in B, and multiply the remainder by twenty. The product represents, approximately, the percentage of quinine, containing one molecule of water.

The explanation of the above processes is this: By the action of ammonia water the cinchona alkaloids are set free and become dissolved in the alcoholic chloroform used for extraction of the bark. The liquid also acts, however, as a solvent upon other substances, for which reason the impure alkaloids are purified by dissolving the mass in acidified water, liberating the alkaloids by caustic potash and extracting them by means of chloroform.

While the direct evaporation of this chloroform solution gives the weight of the total alkaloids, a separation of quinine from the other cinchona alkaloids is accomplished by ether, in which quinine is much more soluble than the rest of the alkaloids. In order to accomplish the extraction with ether successfully the chloroformic solution is made to evaporate over glass powder, by which process the intimate adhering of the alkaloidal particles is prevented. The residue in capsule A contains practically all the quinine, together with a portion of the alkaloids less soluble in ether; the residue in B consists almost entirely of these alkaloids, and as about an equal quantity of them is contained in A and B, the weight of B is deducted from that of A.

Quinine, Quinina, $C_{20}H_{24}N_2O_2.3H_2O = 378$. This formula represents the official alkaloid, but it is also known anhydrous, and in combination with either one or two molecules of water. The anhydrous quinine is a resinous substance, whilst the crystallized quinine is a white, flaky, amorphous or crystalline powder, having a very bitter taste and an alkaline reaction. It is nearly insoluble in water, but soluble in alcohol, ether, ammonia water, chloroform, and dilute acids. When heated to about 57° C. (134° F.) it melts; at 100° C. (212° F.) it loses 2 molecules of water, the remainder being expelled at 125° C. (257° F.).

Quinine sulphate, Quininæ sulphas, $(C_{20}H_{24}N_2O_2)_2H_2SO_4.7H_2O = 872$. This salt, containing two molecules of the alkaloid in combination with one of sulphuric acid and seven of water, is the common form of sulphate of quinine. It forms snow-white, silky, light and fine, needle-shaped crystals, fragile and somewhat flexible, making a very light and easily compressible mass; it has a very bitter taste and a neutral reaction; it is soluble in 740 parts of cold and in 30 parts of boiling water, soluble in 65 parts of alcohol, but nearly insoluble in ether and chloroform; it readily dissolves in diluted sulphuric or hydrochloric acid.

Quinine bisulphate, Quininæ bisulphas, $C_{20}H_{24}N_2O_2.H_2SO_4.7H_2O = 548$. This salt is formed when the common sulphate is dissolved in an excess of diluted sulphuric acid. It crystallizes in colorless, silky needles, has a strongly acid reaction, and is soluble in 10 parts of water.

Quinine hydrochlorate, $C_{20}H_{24}N_2O_2.HCl\ 2H_2O = 396.4$
Quinine hydrobromate, $C_{20}H_{24}N_2O_2.HBr.2H_2O = 440.8$
Quinine valerianate, $C_{20}H_{24}N_2O_2.C_5H_{10}O_2.H_2O = 444.$

The above three salts are obtained by dissolving quinine in the respective acids; they are white, crystalline substances; the first two are easily, the valerianate is sparingly soluble in water.

Iron and quinine citrate is a scale compound obtained by dissolving ferric hydroxide and quinine in citric acid, evaporating, etc.

Analytical reactions:

1. Quinine or its salts, dissolved in water or in dilute acids, give, after having been shaken with fresh chlorine water, or bromine water, an emerald-green color on the addition of ammonium hydroxide. (Plate VII., 4.)

The reaction is readily shown by treating 10 c.c. of a solution (about 1 in 1500) with 2 drops of bromine water, and then with an excess of ammonia water. The green color is due to the formation of thalleioquin.

2. Solutions of quinine, treated with chlorine water, then with fragments of potassium ferrocyanide, turn pink, then red on the addition of ammonium hydroxide not in excess.

3. Solutions of quinine give with water of ammonia a white precipitate of quinine, which is readily dissolved in an excess of ammonia. The precipitate is also soluble in about twenty times its own weight of ether (the other cinchona alkaloids requiring larger proportions of ether for solution).

4. Most solutions of quinine, especially when acidulated with sulphuric acid, show a vivid blue fluorescence.

5. Neutral solutions of quinine are precipitated by alkaline oxalates.

6. Quinine and its salts form colorless solutions with concentrated sulphuric acid. A dark or red color indicates the presence of other organic substances.

Quinidine, $C_{20}H_{24}N_2O_2$. Isomeric with quinine; it gives, like the latter, a green color with chlorine water and ammonia, and forms fluorescent solutions. Unlike quinine, it is precipitated from neutral solutions by potassium iodide. The sulphate is official.

Cinchonine, Cinchonina, $C_{19}H_{22}N_2O = 308$. This alkaloid is found in cinchona bark in quantities varying from 0.5 to 3 per cent. It crystallizes without water, forming white needles; it is almost insoluble in water, soluble in 116 parts of alcohol or in 163 parts of chloroform, readily soluble in dilute acids.

By dissolving the alkaloid in sulphuric acid is obtained:

Cinchonine sulphate, *Cinchoninæ sulphas*, $(C_{19}H_{22}N_2O)_2H_2SO_4.2H_2O$. It is a white, crystalline substance. Cinchonine differs from quinine by its greater insolubility in ether, by its insolubility in ammonia water, by not forming fluorescent solutions, and by not giving a green color with chlorine water and ammonia.

Analytical reactions:

1. Chlorine water added to the solution of a cinchonine salt produces a yellowish-white precipitate insoluble in excess of ammonia.

2. Potassium ferrocyanide solution added to a neutral solution of cinchonine produces a white precipitate soluble in excess of the reagent. Upon adding an acid to this solution a golden-yellow precipitate is formed.

3. With alkali hydroxides, carbonates, and bicarbonates, cinchonine salts form white precipitates insoluble in ammonia.

Cinchonidine, $C_{19}H_{22}N_2O$. An alkaloid isomeric with cinchonine; soluble in 75 times its weight in ether. The sulphate is official.

A mixture of equal parts of sugar and cinchonidine sulphate heated in a dry test-tube causes a deposit of red oily drops on the cool portion of the tube. The addition of 4 c.c. of a saturated aqueous solution of phenol to 1 c.c. of a saturated aqueous solution of cinchonidine sulphate causes a copious deposit of small crystals.

Strychnine, Strychnina, $C_{21}H_{22}N_2O_2 = 334$. This alkaloid is found, together with brucine, in the seeds and bark of different varieties of Strychnos, and is generally obtained from nux vomica. Strychnine is a white, crystalline powder, having an intensely bitter taste, which is still perceptible in solutions containing 1 in 700,000. It is nearly insoluble in water and in ether, soluble in chloroform and in dilute acids.

By dissolving it in sulphuric acid the official *strychnine sulphate, Strychninæ sulphas,* $(C_{21}H_{22}N_2O_2)_2.H_2SO_4.5H_2O$, is obtained.

Strychnine has strong basic properties and is one of the most powerful poisons known, one-quarter of a grain having caused death within a few hours.

Analytical reactions:

1. Strychnine dissolves in sulphuric acid and nitric acid without color.

2. A fragment of potassium dichromate, drawn through a solution of strychnine in concentrated sulphuric acid, produces momentarily a blue, then brilliant violet color, which slowly passes to cherry-red, then to rose-pink, and finally to yellow. This reaction may still be noticed with $\frac{1}{50000}$ grain of strychnine (Plate VII., 5).

3. *Sonnenschein's test.* When to a very small quantity of strychnine, dissolved in a drop of sulphuric acid, some ceroso-ceric oxide is added, and the mixture is stirred with a glass rod, a deep-blue color

is produced, changing soon to violet, and finally remaining cherry-red. One part of strychnine in one million parts of water can thus be recognized. The reagent may be made by heating cerium oxalate to redness and dissolving it in 30 times its weight of sulphuric acid.

4. Solutions of strychnine give with diluted solution of potassium dichromate a yellow, crystalline precipitate, which, when collected, washed, and heated with concentrated sulphuric acid, shows the play of colors described in test 2.

5. Neutral solutions of strychnine give yellow precipitates with the chlorides of gold and platinum and with picric acid; a white precipitate with mercuric chloride, potassium hydroxide, and with chlorine water; a greenish-yellow precipitate with potassium ferrocyanide.

If to the last-named precipitate, after careful decantation of the liquid, sulphuric acid is added, a similar play of colors is produced as stated in reactions 2 and 3.

Brucine, $C_{23}H_{26}N_2O_4.4H_2O$. This alkaloid is found associated with strychnine in various species of Strychnos. It is readily soluble in alcohol, amyl alcohol, and chloroform, but sparingly soluble in cold water and in ether.

Analytical reactions:

1. To 1 c.c. of water add 5 drops of nitric acid and 5 milligrammes of brucine; a deep blood-red color results. Heat the liquid until it has assumed a yellow color, then add 9 c.c. of cold water and a few milligrammes of sodium thiosulphate (or a small crystal of stannous chloride); a beautiful amethyst or violet color results (Plate VII., 6).

2. Fresh chlorine water, added drop by drop to a concentrated brucine solution, produces a red color, turning violet, and becoming colorless on addition of an excess of chlorine.

Atropine, Atropina, $C_{17}H_{23}NO_3 = 289$ (*Daturine*). Occurs in Atropa belladonna. It is a white, crystalline powder, having a bitter and acrid taste and an alkaline reaction; it is sparingly soluble in water, but very soluble in alcohol and chloroform. *Atropine sulphate,* $(C_{17}H_{23}NO_3)_2.H_2SO_4$, is a white, crystalline powder, easily soluble in water.

Analytical reactions:

1. Atropine dissolves in concentrated sulphuric acid without color.

2. The above solution is not colored by nitric acid (difference from morphine), and not at once by potassium dichromate (difference from

strychnine). Prolonged contact with potassium dichromate causes the solution to turn green.

3. The green solution obtained by the action of potassium dichromate upon atropine which has been dissolved in sulphuric acid, evolves on the addition of a few drops of water and warming, a pleasant odor reminding of roses and orange flowers. A similar odor may be noticed when a fragment of atropine is heated slowly in a dry test-tube until it fuses and white fumes begin to appear, heating this mass with a few drops of concentrated sulphuric acid until it commences to turn brown, and then adding at once, but carefully, about two volumes of water.

4. Solutions of atropine dilate the pupil of the eye to a marked extent.

5. One milligramme of atropine, mixed well with an equal weight of sodium nitrate and 3 drops of sulphuric acid, gives a yellowish-red mixture, which turns violet on adding 5 milligrammes of powdered sodium hydroxide and a drop of alcohol.

Hyoscyamine, $C_{17}H_{23}NO_3$. Found in small quantities together with hyoscine in the seeds of Hyoscyamus niger (henbane), and in some other plants belonging to the solanaceæ.

Hyoscyamine resembles atropine closely in most of its chemical, physical, and physiological properties, but the corresponding salts of the two alkaloids crystallize in different forms; the hydrobromate and sulphate are official.

Hyoscyamine differs from atropine by yielding with gold chloride a precipitate which, when recrystallized from a hot aqueous solution, acidified with hydrochloric acid, deposits lustrous, golden-yellow scales.

Hyoscine, $C_{17}H_{21}NO_4$. Found together with hyoscyamine in Hyoscyamus. The alkaloid is known only in an amorphous, semisolid state, but the salts, of which the hydrobromate is official, crystallize readily. Hyoscine evaporated to dryness on a water-bath with a few drops of fuming nitric acid leaves a nearly colorless residue which turns violet on the addition of some alcoholic solution of potassium hydroxide.

Cocaine, $C_{17}H_{21}NO_4$. This alkaloid is found in the leaves of the South American shrub Erythroxylon coca in quantities varying from 0.15 to 0.65 per cent. It is a white, crystalline powder, soluble in about 700 parts of water, easily soluble in alcohol, ether, and chloroform; it fuses at 98° C. (208° F.). A fragment of cocaine placed on the tongue causes the sensation of numbness without acrid or bitter taste; the solution in water is faintly bitter.

Cocaine heated with acids in sealed tubes is decomposed into methyl alcohol, benzoic acid, and *ecgonine,* showing it to be methyl-benzoyl-ecgonine:

$$\underset{\text{Cocaine.}}{C_{12}H_{21}NO_4} + 2H_2O = \underset{\text{Methyl alcohol.}}{CH_3HO} + \underset{\text{Benzoic acid.}}{C_7H_5CO_2H} + \underset{\text{Ecgonine.}}{C_9H_{15}NO_3}.$$

Ecgonine is found in the coca leaves as benzoyl-ecgonine, $C_9H_{15}(C_7H_5O)NO_3 + 4H_2O$; this is a white, crystalline substance from which cocaine may be obtained by heating it with methyl-iodide. The mother-liquors obtained in the manufacture of cocaine from the leaves contain the alkaloid in an amorphous state and possibly one or two other alkaloids, one of which has been named *hygrine.* Whether these alkaloids are contained in the coca-plant, or are products of the decomposition of cocaine, are questions not yet decided.

Of the various salts of cocaine, the hydrochlorate, $C_{17}H_{21}NO_4.HCl$, has been used chiefly. This salt crystallizes from alcohol in short, anhydrous prisms, from an aqueous solution, however, with two molecules of water, which are completely expelled at a temperature of 100° C. (212° F.). The anhydrous salt fuses at 193° C. (379° F.) and is readily soluble in water; this salt solution has a somewhat more bitter taste than the alkaloid itself.

Analytical reactions:

1. Cocaine salts are precipitated from an aqueous solution as follows: Platinum chloride produces a yellowish-white, mercuric chloride a white flocculent, picric acid a yellow pulverulent, the alkali carbonates and hydroxides a white precipitate, which latter is soluble in ammonia.

2. To a freshly prepared solution of potassium ferricyanide add an equivalent amount of ferric chloride; with this solution of ferric ferricyanide moisten a slip of filter-paper and place on this a drop of cocaine solution. A deep-blue spot of ferric ferrocyanide will appear shortly in consequence of the deoxidizing action of the alkaloid upon the ferricyanide. (Morphine, a few other alkaloids, and many reducing agents show the same reaction.)

3. Boil a small quantity of cocaine solution for a few minutes with dilute sulphuric acid; neutralize carefully with potassium hydroxide and then add a few drops of ferric chloride solution. A pale brownish-yellow precipitate of basic ferric benzoate will form.

Aconitine, $C_{33}H_{45}NO_{12}$? This alkaloid is found in various species of aconitum to the amount of about 0.2 per cent. The commercial article is most likely a mixture of aconitine with other substances, as it is extremely difficult to obtain the alkaloid in an entirely pure form; the composition given above corresponds to the analysis of the purest obtainable article. Aconitine is one of the most poisonous substances known; there are no reliable chemical tests by which it may be readily distinguished from other alkaloids; the aqueous solution is precipitated by alkalies, tannic acid, Mayer's reagent, and solution of iodine in potassium iodide, but not by platinic chloride, mercuric chloride, and picric acid. Characteristic is the intensely acrid taste of the alkaloid and the numbness and tingling caused by it in the mouth and throat. The greatest care should be exercised in examining aconitine for these properties.

Veratrine, Veratrina. This is a mixture of alkaloids obtained from the seed of Asagræa officinalis. It is a white, amorphous, rarely crystalline powder, highly irritating to the nostrils; nearly insoluble in water, readily soluble in alcohol.

Analytical reactions:

1. Concentrated sulphuric acid causes with veratrine first a yellow, then reddish-yellow, intense scarlet, and, finally, violet-red color. (Plate VII., 8.) The yellow or orange-red solution exhibits, by reflected light, a greenish fluorescence.
2. Veratrine, when heated with concentrated hydrochloric acid, dissolves with a blood-red color.
3. Bromine water colors veratrine violet.
4. Veratrine forms with nitric acid a yellow solution.

Hydrastine, $C_{21}H_{21}NO_6$. Found together with berberine in the rhizome of hydrastis Canadensis (golden seal) in quantities varying from 0.1 to 0.2 per cent. Hydrastine crystallizes in four-sided, colorless prisms; it fuses at 132° C. (270° F.), is insoluble in water and benzin, soluble in about 2 parts of chloroform, 83 parts of ether, and 120 parts of alcohol at the ordinary temperature.

Hydrastine answers to all the general tests for alkaloids; treated with concentrated sulphuric acid it shows a yellow color, turning red, then purple on heating. Concentrated nitric acid produces a yellow color, changing to orange. The fluorescence noticed in solutions of hydrastine or its salts is due to products formed from it by oxidation. While hydrastine itself crystallizes very readily, especially from solutions in acetic ether, its salts can scarcely be obtained in crystals.

Hydrastinine, $C_{11}H_{11}NO_2$. When hydrastine is treated with oxidizing agents it is converted into hydrastinine, the hydrochlorate of which is official. This salt has a pale-yellow color, a bitter, saline taste, and is soluble in 0.3 part of water, and also readily soluble in alcohol, but difficultly soluble in ether or chloroform. A dilute aqueous solution of the salt (up to about 1 in 100,000) has a decided blue fluorescence.

Berberine, $C_{20}H_{17}NO_4$. Found in a number of plants (berberis vulgaris, hydrastis Canadensis, etc.) belonging to entirely different families. It is a yellow, crystalline substance, soluble in 7 parts of alcohol, 18 parts of water, insoluble in ether, chloroform, and benzene.

Berberine not only forms well-defined, readily crystallizing salts with acids, but it also enters into combination with a number of other substances, as, for instance, with alcohol, ether, chloroform, etc. Some of these compounds crystallize well, as for instance, berberine-chloroform, $C_{20}H_{17}NO_4.CHCl_3$.

Physostigmine, $C_{15}H_{21}N_3O_2$ (*Eserine*). Found in the seeds of Physostigma venenosum (Calabar bean). The pure alkaloid does not crystallize well, is almost tasteless, and assumes gradually a reddish tint. The sulphate and salicylate are official. Both are white or yellowish-white crystalline powders, which have a bitter taste. The sulphate is readily, the salicylate sparingly soluble in water.

Analytical reactions:

1. Five milligrammes of physostigmine dissolved in 2 c.c. of ammonia water yield a yellowish-red liquid which, on evaporation on a water-bath, leaves a blue or bluish-gray residue, soluble in alcohol, forming a blue solution. Upon supersaturation with acetic acid this becomes violet and exhibits a strong reddish fluorescence. The violet solution leaves on evaporation a residue which is first green and afterward blue. (Plate VII., 7.)

2. Physostigmine or its salts give with calcium oxide and water a red liquid, which turns green on heating.

Pilocarpine, $C_{11}H_{16}N_2O_2$. Found in the leaflets of Pilocarpus Selloanus. The alkaloid crystallizes with difficulty; its solutions in ether, alcohol, or water have an alkaline reaction. The hydrochlorate is official. It is a white, crystalline powder, which dissolves in fuming nitric acid with a faintly greenish tint. The aqueous solution is precipitated by most of the common reagents for alkaloids.

Caffeine, Caffeina, $C_8H_{10}N_4O_2.H_2O = 212$ (*Trimethyl-xanthine, Theine, Guaranin*), occurs in coffee, tea, Paraguay tea, and a few other plants. It forms fleecy masses of long, flexible, silky needles, which are soluble in 80 parts of water and in 33 parts of alcohol; it has a slightly bitter taste and a neutral reaction.

Caffeine and theobromine show the properties of alkaloids to a much less degree than the majority of the compounds considered in this chapter; they do not act on red litmus and are but feebly basic.

Citrated caffeine U. S. P. is obtained by adding caffeine to a solution of citric acid and evaporating the mixture to dryness.

Caffeine is dissolved by sulphuric acid without color; when treated with strong nitric acid it forms a yellow liquid which, after evaporation, assumes a purplish color when moistened and carefully heated with water of ammonia.

Two volumes of a saturated solution of caffeine in water mixed with one volume of mercuric chloride solution form after a short time large crystals of caffeine-mercuric chloride.

Theobromine, $C_7H_8N_4O_2$ (*Dimethyl-xanthine*). Found in the seeds of Theobroma cacao, a tree growing in the tropics. It is white, crystalline, sparingly soluble in cold water, alcohol, and ether, volatilizes without decomposition at 290° C. (554° F.), has a neutral reaction, but forms with acids well-defined salts.

Theobromine has been obtained from xanthine, $C_5H_4N_4O_2$ (a base found in animal liquids), by treating its lead compound with methyl-iodide, CH_3I, when lead iodide and dimethyl-xanthine are formed. By introducing a third methyl group into the molecule of theobromine trimethyl-xanthine, *i. e.*, caffeine or theine is formed. These facts show the close relationship between the active principles of the vegetable substances used so extensively in the preparation of the beverages, coffee, tea, and chocolate. And again, these principles show a relationship to a series of substances (such as xanthine, uric acid, and others) which are found in animal fluids.

Piperin, $C_{17}H_{19}NO_3$. This compound is found in black and white pepper. While it is isomorphous with morphine, it differs widely from it in all its properties. It can hardly be called an alkaloid, as it has no alkaline reaction, is but feebly basic and does not show the general alkaloidal reactions. It forms colorless, or pale yellowish crystals which are, when first put in the mouth, almost tasteless, but produce on prolonged contact a sharp biting sensation.

Piperin dissolves in concentrated sulphuric acid with a dark blood-red color, which disappears on dilution with water. Treated with nitric acid it turns rapidly orange, then red.

Ptomaines (*Putrefactive or cadaveric alkaloids*). It has been known for a long time that vegetable, and more especially animal matter, when in a state of decomposition (putrefaction) acts generally as a poison, both when taken as food or when injected under the skin. Though many attempts had been made to isolate the poisonous products, this was not accomplished successfully until the years 1873 to 1876, by Francesco Selmi, of Italy. He demonstrated that a great number of basic substances can be extracted from putrid matter by treating it successively with ether, chloroform, amyl alcohol, and other solvents. He also showed that these substances resemble vegetable alkaloids in many respects, and assigned to them the name ptomaines, derived from πτῶμα, that which is fallen—*i. e.*, a cadaver.

Although Selmi did not succeed in isolating any of the ptomaines completely (he experimented with extracts only) his investigations stimulated other scientists, and by the united efforts of many workers our knowledge of ptomaines has now advanced so far, that general statements can be given in regard to their origin, composition, physical and chemical properties, action upon the animal system, etc.

Formation of ptomaines. It has been shown in Chapter 39 that albuminous substances under favorable conditions undergo a decomposition termed putrefaction. Presence of moisture, a suitable temperature, and the action of a ferment are the essential factors in putrefaction. The ferments are living organized beings, termed germs, bacteria, bacilli, microbes, organized ferments, etc.

It is during the growth, development, and multiplication of these micro-organisms that the decomposition of the albuminous substances into simpler forms of matter takes place. A full explanation of the exact mode of the formation of decomposition-products from organic matter by the action of bacteria has not been furnished yet, but we do know that ptomaines are found among these products. We also know that certain bacteria split up organic molecules in a certain direction, *i. e.*, with the formation of certain products. We also know that while micro-organisms live chiefly in dead organic matter, they also have the power of existing and multiplying in the living organism, causing the decomposition of living tissues, often with the formation of ptomaines.

General properties of ptomaines. Ptomaines resemble vegetable alkaloids in all essential properties. Some contain carbon, hydrogen, and nitrogen only, corresponding to the volatile alkaloids, such as coniine and nicotine, while others contain oxygen also, corresponding to the fixed alkaloids.

Ptomaines and alkaloids both have the basic properties and the power to combine with acids to form well-defined salts; they have in common a number of characteristic reactions, such as the formation of precipitates with the chlorides of platinum, mercury, gold, as also with tannic acid, phospho-molybdic acid, picric acid, etc.; and both show corresponding solubility and insolubility in the various solvents generally used for the extraction of alkaloids.

Ptomaines not only possess the general characters of true alkaloids, but even the often highly characteristic color-tests of the latter are in some cases almost identical with those of ptomaines. Thus, ptomaines have been found which resemble in their chemical properties as well as in their physiological action upon the animal system, the alkaloids morphine, atropine, strychnine, coniine, digitaline, etc.

Many attempts have been made to find some characteristic properties by which to differentiate between the putrefactive and the vegetable alkaloids, but practically without results. It is true that most vegetable alkaloids are optically active, while ptomaines are inactive, but it does not often happen that ptomaines are obtained in such quantities as to permit of an exact determination of optical properties.

Under these conditions it is evident that the toxicologist has a most difficult task, when called upon to examine a body (especially when already in a state of decomposition) for alkaloidal poisons. How many times, in former years, chemists may have unjustly claimed the presence of poisonous vegetable alkaloids in material given them for examination, we cannot say, but we do know of a number of cases of recent date in which such claims were shown to be based upon errors, made in consequence of the close analogy between ptomaines and alkaloids.

While the poisonous properties of some ptomaines are well marked, others are more or less inert. The poisonous ptomaines are now often termed *toxines,* in order to distinguish them from the inert basic products of putrefactive changes.

The toxines are of special interest to the physician, because it is now assumed that *infectious diseases are caused by the poisonous products formed by the growth, multiplication, and degeneration of micro-organisms in the living body.*

The great likelihood of this statement is of far-reaching importance, as it opens a new field for investigation in connection with the treatment of infectious diseases.

Non-poisonous ptomaines. A number of these basic substances have been known for a long time. Some of them are also formed by other processes than those of putrefaction, and the term ptomaines may, therefore, not well be chosen for all of them. However, the close relationship between these substances unites them into a natural group, of which the following members may be mentioned:

Methylamine, $NH_2.CH_3$, the simplest organic base that can be formed, has been found in decomposing herring, pike, haddock, poisonous sausage, cultures of comma bacillus on beef-broth, etc. It is an inflammable gas of strong ammoniacal odor.

Dimethylamine, $NH(CH_3)_2$, has been found in putrefying gelatin, decomposing yeast, poisonous sausage, etc. It is, like the former, a gas at ordinary temperature.

Trimethylamine, $N(CH_3)_3$, has been shown for a long time to occur in some animal and vegetable tissues. Its presence has been demonstrated in leaves of chenopodium, in the blood of calves, in human urine, etc., but it also occurs as a product of putrefaction in yeast, meat, blood, ergot, etc. It is a liquid, possessing a strong, fish-like odor. Boiling-point 9° C. (48° F.).

Ethylamine, $NH_2.C_2H_5$; *Diethylamine,* $NH.(C_2H_5)_2$; *Triethylamine,* $N.(C_2H_5)_3$; *Propylamine,* $NH_2.C_3H_7$; *Neuridine,* $C_5N_2H_{14}$, are other non-poisonous volatile ptomaines belonging to the amine group, while of the non-volatile amides may be mentioned: *Mydine,* $C_8H_{11}NO$; *Pyocyanine,* $C_{14}H_{14}NO_2$; *Betaine,* $C_5H_{13}NO_3$, etc.

Poisonous ptomaines. While no strict line of demarcation can be drawn between poisonous and non-poisonous substances, the following list of ptomaines embraces those which cause serious disturbances when brought into the animal system:

Isoamylamine, $C_5H_{13}N$, a colorless, strongly alkaline liquid, has been found in putrefying yeast and in cod-liver oil. It is strongly poisonous, producing rigor, convulsions, and death.

Cadaverine, $C_5H_{14}N_2$, occurs very frequently in decomposing animal tissues, and seems to be a constant product of the growth of the comma bacillus, irrespective of the soil on which it is cultivated. It is a syrupy liquid, possessing an exceedingly unpleasant odor, resembling that of coniine. The substances which have been described by various scientists as "animal coniine" were most likely cadaverine. This base is not very poisonous, but is capable of producing intense inflammation, necrosis, and suppuration in the absence of bacteria.

Neurine, $C_5H_{13}NO$, is a base which has been obtained by boiling protagon with baryta, and has been formed by synthetical processes. It also occurs, however, frequently in decomposing meat. It is exceedingly poisonous, even in small doses. Atropine possesses a strong antagonistic action toward neurine, and the injection of even a small quantity is sufficient to dispel the symptoms of poisoning by neurine.

Choline, $C_5H_{15}NO_2$, has been found in animal tissues, in a number of plants (hops, ergot, Indian hemp, white mustard, etc.), and in putrid matters. It is much less poisonous than neurine.

Mytilotoxine, $C_6H_{15}NO_2$, is the poison found in poisonous mussels. It has a strong paralysis-producing action, resembling curara in that respect.

Typhotoxine $C_7H_{17}NO_2$, is looked upon as the specific toxic product of the activity of Koch-Eberth's typhoid bacillus. The poison throws animals into a paralytic or lethargic condition, so that they lose control over the muscles and fall down helpless. Simultaneously frequent diarrhœic evacuations take place, and death follows in from one to two days.

Tetanine, $C_{13}H_{30}N_2O_4$, has been obtained from cultures of tetanus microbes, from the amputated arm of a tetanus patient, and from the brain and nerve tissues of persons who died from tetanus. It produces in animals the symptoms characteristic of tetanus, such as tonic and clonic convulsions. While mice and rabbits are strongly affected by tetanine, dogs and horses seem to be but slightly susceptible to its action.

Mydatoxine, $C_6H_{13}NO_2$, has been obtained from human internal organs which were kept for four months at a temperature varying from $-9°$ to $+5°$ C. (16° to 41° F.). It is an alkaline syrup, which does not possess strong toxic properties.

Tyrotoxicon. The composition of this highly poisonous ptomaine has not been established yet. It has been found in decomposing milk, in poisonous cheese, ice-cream, and cream-puffs.

Spasmotoxine. Composition yet unknown. Obtained from cultures of the tetanus-germ on beef-broth. Produces violent convulsions.

Leucomaines. The basic substances formed in the living tissues by retrograde metamorphosis, during normal life, are known as leucomaines, in contradistinction to the ptomaines, or basic products of putrefaction. To the group of leucomaines belong many substances known long ago, such as creatine, creatinine, xanthine, guanine, and others. Most of these bodies are non-poisonous, but some have been discovered of late, possessing strong poisonous properties. The more important leucomaines will be mentioned in the physiological part.

Bacterial proteids or toxalbumins. Of even a more recent date than the discovery of ptomaines is that of bacterial proteids, a group of substances of which but little is known so far. They are formed by the action of micro-organisms upon albuminous matter. The isolation of these substances is extremely difficult, because they differ but little in solubility or other physical and chemical properties from the normal proteids; and, moreover, they decompose so readily that they may disappear during the process of analysis. Some of the bacterial proteids show the Millon and biuret reactions characteristic of albuminous substances; they are also precipitated by tannic acid, picric acid, and mercuric chloride.

Of bacterial proteids which have been isolated may be mentioned the *proteid poison of diphtheria.* This substance has been obtained as a white, amorphous powder from cultures of the Loeffler diphtheria bacillus. The poisonous properties of this substance are very intense, as 0.2 milligramme suffices to kill a rabbit. The symptoms produced by the poison, when injected into susceptible animals, are identical with those produced by inoculation with the living bacillus.

Other poisonous proteids have been obtained from cultures of the tetanus bacillus, of the comma bacillus (found in cholera patients), of the Eberth bacillus (found in typhoid-fever patients), and from micro-organisms found in the intestines and stools of children suffering from summer diarrhœa. The proteids in the latter case are highly poisonous, causing, when injected under the skin of dogs, vomiting, purging, collapse, and death.

Antitoxins. After an infectious disease has passed over, there are present in the system, as a result of the action of the micro-organisms upon the tissues of the body, certain substances which have the power of protecting the individual to a certain extent against other attacks of the same disease. These bodies are known as antitoxins; their chemical composition is yet unknown. By some they are considered albumins, by others globulins; still others claim them to be nucleins.

The antitoxins are found in the blood-serum of the animals which have recovered from an infectious disease, and this serum may be utilized in the treatment of the same disease in other individuals, and in even rendering immune others susceptible to that disease. (Blood-serum therapy of Behring.) Practically, animals such as cows, horses, dogs, goats, are rendered highly immune to such diseases as tetanus and diphtheria by injecting them with attenuated cultures of the micro-organisms (causing these diseases) or their toxins, and then with gradually increasing doses of virulent cultures until the animals become highly refractory to these diseases. The blood-serum of such animals is now extensively used with remarkable success in the treatment of tetanus and diphtheria.

51. PROTEIDS (ALBUMINOUS SUBSTANCES).

Occurrence in nature. Proteids form the chief part of the solid and liquid constituents of the animal body; they occur in blood,

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Questions.—491. State the general physical and chemical properties of alkaloids. 492. Give a general method for the extraction and separation of alkaloids from vegetables. 493. Mention the chief constituents of opium, and explain the process for determining the percentage of morphine in opium. 494. Mention the properties of morphine and its salts; give tests for them. 495. Mention the principal alkaloids found in cinchona bark, and give a process by which the total quantity of these alkaloids and of quinine may be determined. 496. State the physical and chemical properties of quinine and cinchonine. Which of their salts are official, and by what tests may these alkaloids be recognized and distinguished from each other? 497. Give tests for strychnine, brucine, atropine, and veratrine. 498. What is the chemical relationship between xanthine, caffeine and theobromine? 499. Mention properties of and give tests for cocaine. 500. Mention the characteristic physical, chemical, and physiological properties of ptomaines.

tissues, muscles, nerves, glands, and all other organs; they are also found in small quantities in nearly every part of plants, and in larger quantities in many seeds. They have never yet been formed by artificial means, but are almost exclusively products of vegetable life, and undergo but little change when consumed as food and assimilated by animals.

General properties. The various proteids resemble one another closely in their properties. Their composition is so complex that, as yet, no chemical formula has been assigned to them with any certainty, The percentage composition and other reasons have led to a formula represented by $C_{144}H_{224}N_{36}O_{44}S_2$, which represents about the average composition of the proteids. The percentage composition is shown in the following figures:

Carbon	50.0 per cent.	to	55.0	per cent.
Hydrogen	6.7 "	"	7.3	"
Nitrogen	15.0 "	"	18.2	"
Oxygen	20.0 "	"	24.0	"
Sulphur	0.3 "	"	2.5	"

Of other properties may be mentioned:

1. They are amorphous, colorless, odorless, nearly tasteless substances, and, with the exception of peptones, incapable of dialysis.

2. They are not volatile without decomposition.

3. They easily undergo that decomposition known as putrefaction.

4. Some are soluble in water, others only in water containing alkalies, acids, or certain neutral salts, whilst some are insoluble.

5. The soluble proteids are converted into insoluble modifications either by heating to 60° or 70° C. (140° or 158° F.), or by the addition of mineral acids, alcohol, or certain metallic salts. This process of converting soluble into insoluble proteids is called *coagulation;* and proteids when once coagulated will not return to their original soluble form without suffering some alteration.

6. They are converted into peptones by the action of gastric juice. (See later.)

Analytical reactions.

(Use a solution made by dissolving some of the white of an egg in about 10 parts of water, and filtering.)

1. Proteids or their solutions are colored yellow by warm nitric acid in consequence of the formation of a substance called xanthoproteic acid. Addition of ammonia water changes the yellow color to orange or red.

2. *Millon's reagent* colors them purple-red on heating. This reagent is a solution of mercuric nitrate, containing some excess of nitric acid; it is best made by dissolving 1 part of mercury in 2 parts of nitric acid of a specific gravity of 1.42, and diluted with 2 volumes of water.

3. *Biuret-reaction.* A few drops of dilute cupric sulphate solution and then an excess of potassium hydroxide added, give a violet color.

4. Heating of equal volumes of proteid solution and a saturated aqueous solution of ammonium sulphate causes the precipitation of all proteids except that of peptones.

5. A few drops of solution of 1 part of cane sugar in 4 parts of water and then strong sulphuric acid added, produce a purple color.

6. They are often precipitated by highly diluted acids, but redissolved by boiling with strong hydrochloric acid, forming a violet-red solution. The precipitated proteids are also generally dissolved by caustic alkalies.

7. They are also precipitated by tannin, carbolic and picric acids, by potassium ferrocyanide and acetic acid, by lead acetate, mercuric chloride, and by most salts of heavy metals. (The use of egg-albumin in cases of poisoning by metallic compounds depends on this property.)

Classification. Our present unsatisfactory state of knowledge regarding proteids, the close resemblance which they show in properties, and the difficulties which are met with in separating them in a pure state, make it difficult to arrange these bodies properly. However, eight classes are now generally distinguished. They are: I. Native or true albumins; II. Globulins; III. Derived albumins or albuminates; IV. Fibrins; V. Coagulated proteids; VI. Albumoses; VII. Peptones; VIII. Amyloid substance or Lardacein.

Class I. Native or true albumins. These proteids are soluble in pure water; the solutions become turbid at 60° C. (140° F.), and are coagulated, especially in presence of a dilute acid, at or below 75°C. (167° F.). Strongly alkaline solutions are not precipitated by heating, and the presence of too much free acid may also prevent coagulation. Coagulated albumin is dissolved by strong solutions of alkali hydroxides. Native albumins occur in the whites of birds' eggs, in milk, in the plasma of the blood, chyle, lymph, etc., as also in plants.

a. Serum-albumin is found dissolved in blood-serum (in human blood to the extent of about 4 to 5 per cent.), in lymph, chyle, transudations, and, in very small quantities, in milk. Pathologically it occurs in urine. Obtained from blood-serum by saturating it at 30° C. (86° F.) with magnesium sulphate, which precipitates globulin; the filtered solution is saturated at 40° C. (104° F.) with sodium sulphate, when the serum-albumin is precipitated. Thus obtained, it is not quite pure, but contains some salts which may be eliminated by dissolving the precipitate in water and subjecting the solution to dialysis.

Pure serum-albumin is an almost white, or pale-yellow, elastic substance, dissolving readily in water to a slightly alkaline, opalescent solution, which coagulates by heating to 50° C. (122° F.), while the addition of sodium chloride raises the coagulating-point to 75°–80° C. (167°–176° F.). It is not readily coagulated by alcohol or precipitated by ether. It turns the plane of polarized light to the left.

b. Egg-albumin differs but little from the former, but may be distinguished from it by being coagulated by ether, which does not affect serum-albumin. It exists in solution in the white of eggs, where it is contained in a network of delicate membranes.

c. Vegetable albumin exists in nearly all vegetable juices, and is a valuable constituent of vegetables used as food. It is coagulated at 61°–63° C. (142°–146° F.), and by nearly all acids.

Class II. Globulins. They are, like native albumins, coagulated by heat, but differ from them by not being soluble in pure water; they are soluble in dilute solutions of neutral salts of the alkalies or alkaline earths (such as sodium or potassium chloride, sodium or magnesium sulphate, etc.), but are in most cases precipitated by saturated solutions of the salts mentioned, as also by passing a current of carbon dioxide through their solutions.

a. Paraglobulin or Serum-globulin. This substance is found in considerable quantity in blood-serum, constituting about one-half of its total proteids; it also occurs in lymph. The most satisfactory method of preparing paraglobulin is to saturate blood-serum with magnesium sulphate at a temperature of 30° C. (86° F.), when it is precipitated and purified by washing it upon a filter, first with a solution of magnesium sulphate, and then with water. Paraglobulin shows the general properties mentioned above as characteristic of globulins.

b. Fibrinogen is the name given to a substance found in blood-plasma, chyle, lymph, and other coagulable fluids of the body. On contact with a peculiar ferment (fibrin-ferment), it is converted into fibrin, thereby giving rise to the phenomenon of coagulation.

Fibrinogen may be obtained by allowing blood to run directly from the vessels into a weak solution of magnesium sulphate, then separating the corpuscles, and precipitating the fibrinogen by saturating the solution with sodium chloride. The precipitate is collected on a filter and purified by dissolving it in an 8 per cent. solution of sodium chloride, and reprecipitating it by again saturating the solution with the salt.

c. *Myosin.* Living muscular tissue contains a yellowish, opalescent fluid (muscle-plasma), which filters with difficulty and clots at temperatures above 0° C. (32° F.). This clotting or coagulation of muscle-plasma also takes place after death and gives rise to the condition known as *rigor mortis.* This change is similar to the formation of fibrin in the blood and possibly due to the action of a myosin ferment.

Myosin is obtained by extracting muscular tissue with 10 per cent. solution of ammonium chloride (in which it is readily soluble) and precipitating it from this solution by the addition of large quantities of water.

Aside from the general reactions characteristic of globulins it is distinguished by the low temperature of 40° to 50° C. (104° to 122° F.), at which it coagulates when dissolved in salt solutions.

d. *Crystallin and Vitellin* are globulins which resemble one another so closely that they may be identical. Crystallin occurs in crystalline lenses to the extent of nearly 25 per cent.; vitellin is found in the yolk of hens' eggs to the amount of about 15 per cent. Both substances are white, flaky solids, readily soluble in dilute acids and alkalies, and also in a 10 per cent. solution of sodium chloride. The latter solution is coagulated by heating to 75° C. (167° F.).

Class III. Derived albumins or albuminates. These substances are insoluble in water, and in dilute neutral salt solutions; soluble in dilute acids and alkalies. Solution not coagulated on heating.

a. *Acid-albumins.* When the solution of a native albumin, such as serum- or egg albumin, is treated for some little time with a dilute acid (hydrochloric acid) its properties become entirely changed. Thus: the solution is no longer coagulated by heat, and on neutralizing it carefully the whole of the albumin is precipitated. This shows that the native albumin, which is soluble in water and in neutral salt solutions, has been changed into a form insoluble in these agents, and this modified form is termed acid-albumin. Acid-albumins, while insoluble in water and in neutral salt solutions, are readily dissolved by dilute acids, and also by diluted alkaline solutions, most likely with conversion into alkali-albumins.

b. Syntonin is the name given to the acid-albumin obtained by digesting myosin with very weak (0.1 to 0.2 per cent.) hydrochloric acid. From the solution thus formed it is precipitated by neutralizing with an alkali; it is soluble in lime-water and in dilute solution of sodium carbonate. Syntonin represents the first stage in the action of gastric juice upon the proteids. It is a pasty, whitish substance, possessing the solubilities mentioned above for acid-albumins.

c. Alkali-albumins. Obtained by treating the different proteids with alkalies and precipitating the solution by neutralizing with an acid. They resemble acid-albumins in many respects, dissolve very slightly in water, neutral salt solutions, and also in lime-water.

d. Casein. This proteid, which resembles alkali-albumin closely, is found in milk, but in no other fluid or secretion of the body. It is best obtained by diluting milk with about 4 volumes of water and acidulating the mixture with acetic acid until it contains about 0.1 per cent. of this acid. Casein can also be precipitated from milk by the addition of sodium chloride or magnesium sulphate.

Pure casein is a fine, snow-white powder, insoluble in water, soluble in alkalies, carbonates, and phosphates of the alkalies, and in lime-water. From these solutions it is precipitated by excess of neutral salts (sodium chloride) and by dilute acids, an excess of which redissolves them. It is not coagulated by heat, but by rennet, an enzyme found in gastric juice.

e. Vegetable casein or *Legumin* occurs in considerable quantities in the seeds of leguminosæ, such as peas and beans, which contain nearly 25 per cent.; it is also found in almonds, various nuts, etc. It shows reactions very similar to milk-casein.

Class IV. Fibrins. Insoluble in water; soluble with difficulty in strong acids and alkalies, and undergoing a simultaneous change into members of Class III. Coagulated by heat.

a. Blood-fibrin does not exist as such in the body, but is produced during the process of clotting of blood, lymph, chyle, and other coagulable fluids of the body. The formation is due to the action of the fibrin-ferment (of which but little is known) upon fibrinogen and possibly a second substance, fibrinoplastin. It may be obtained unstained by the red corpuscles (as it is in a common blood-clot) by whipping fresh blood with a bundle of twigs and then washing with water. It is, when recently obtained, a white, gelatinous, tenacious mass, consisting of numerous minute fibrils. When dried it becomes hard and brittle. It is insoluble in water, alcohol, and ether, but swells up and dissolves slowly in dilute acids.

b. Vegetable fibrin or *Gluten* exists in many parts of vegetables, and is best obtained from wheat-flour by kneading it on a sieve with water, when the starch passes through and gluten remains as a soft, elastic mass, insoluble in water, alcohol, and ether. It is probably a mixture of several proteids.

Class V. Coagulated proteids. These are formed by the action of heat, acids, alcohols, etc., on solutions of true albumins or globulins. They are insoluble in water, dilute acids and alkalies, as also in neutral salt solutions of any strength. In fact, they are soluble only in strong acids and strong alkalies, when, however, a destructive decomposition takes place. Prolonged contact with dilute acids, especially at high temperatures, also effects a partial solution with decomposition. The most characteristic property of coagulated proteids is that they readily undergo gastric and pancreatic digestion.

Class VI. Albumoses. Intermediary products between acid-albumins and the peptones. The albumoses are at least three in number: protalbumose, hetero-albumose and dextro-albumose. The albumoses are precipitated by a saturated solution of ammonium sulphate, while peptone remains in solution. All are soluble in dilute solution of sodium chloride, and some in water. They differ but slightly from one another, and give a red color with the biuret test.

Class VII. Peptones. These are the products of the action of the gastric and pancreatic juices upon proteids during the process of digestion. They are soluble in water, acids, alkalies, salt solutions, including solution of ammonium sulphate; only precipitated by alcohol, tannic acid, potassium mercuric iodide, and mercuric chloride. They give a red color with the biuret test. Characteristic is that peptones are capable of dialysis, or of diffusion through membranes, whilst proteids are not.

Class VIII. Amyloid substance or Lardacein. This is a pathological product, which is sometimes found in severe wasting diseases, imparting a peculiar translucent appearance to the tissues. Its composition is that of the proteids, but differs from them in being colored red by iodine, violet or blue by iodine and dilute sulphuric acid. It does not undergo putrefaction as readily as other proteids.

Hæmoglobin (*Hæmato-crystallin, Hæmato-globulin*). This substance is the coloring agent of the blood; it resembles the proteids in many respects, but differs from them in being crystallizable and in containing iron. Its composition has been found to correspond to the formula $C_{600}H_{960}N_{154}O_{179}FeS_3$.

The most characteristic feature of a solution of hæmoglobin is its power of absorbing various gases; it absorbs oxygen in considerable quantities, thereby assuming a bright-red color, but gives up the oxygen again when treated with deoxidizing agents. Accordingly, we distinguish between common or reduced hæmoglobin and oxyhæmoglobin; by means of oxidizing and reducing agents, the one body can readily be converted into the other. Solutions of oxyhæmoglobin show a bright-red or scarlet color, those of hæmoglobin are much darker and of a purple tint.

Upon the combination of oxygen with the hæmoglobin of the blood in the lungs, and the deoxidation of the hæmoglobin by the tissues, depends the process of respiration, which will be spoken of later.

Hæmoglobin enters into combination with certain other gases—for instance, carbonic oxide, nitrogen dioxide, and hydrocyanic acid—more readily than with oxygen, and the poisonous properties of these gases are due largely to their power of satisfying the affinities of the hæmoglobin, and in this way rendering it incapable of taking up oxygen.

Hæmoglobin is soluble in water, in dilute solutions of albumin, of the alkalies and their carbonates, and in sodium or ammonium phosphate. It is insoluble in strong alcohol, ether, and in the volatile and fatty oils. With the spectroscope both oxyhæmoglobin and reduced hæmoglobin show characteristic absorption bands.

Hæmoglobin may be obtained in beautiful red crystals, which differ in shape, and solubility in water, according to the species of animal from whose blood they are obtained.

Hæmoglobin may be decomposed by boiling with alcohol (or by other agents) into albumin and a substance called *hæmatin*, $C_{34}H_{35}N_4O_5Fe$, which is soluble in acidified alcohol. Hæmatin is a bluish-black powder, which forms with hydrochloric acid a crystalline compound, *hæmine*, which fact is made use of in a characteristic microscopical test for the presence of blood.

Proteolytic or Hydrolytic ferments. Enzymes. Proteolysis is the change effected in proteids during their digestion, and as this change in most cases is accompanied by the taking up of water, the terms proteolytic or hydrolytic ferments are used for the substances causing the digestive changes. They are also called enzymes, to distinguish them from organized ferments, such as yeast and bacteria. The composition of these compounds is not definitely known, but is similar to that of proteids. Enzymes are present in many secretions and are produced within the body. They are soluble in water and glycerin, but insoluble in alcohol. They act only in the presence of water. They have no power of reproduction and are apparently not diminished in quantity by activity. Each ferment acts upon certain groups of compounds, causing them (in most cases) to take up a molecule of water.

The most important of these unorganized hydrolytic ferments are *ptyalin*, found in saliva; *pepsin* and *rennet ferment*, found in gastric juice; *amylopsin*, *trypsin*, *steapsin*, and a *milk-curdling ferment* found in pancreatic juice; *invertin*, found in intestinal juices; and, finally, a *fibrin-forming ferment*, found in coagulating blood. (For details of most of these ferments, see next chapter).

Pepsin is one of the active principles of gastric juice, capable of converting albumin, in the presence of hydrochloric acid, into soluble peptones. While pure pepsin is not known, a number of preparations containing more or less of this ferment are sold as pepsin. They are obtained by different processes of extraction from the glandular layer of fresh stomachs from healthy pigs.

Pepsin, U. S. P., should be either a fine, white, or yellowish-white, amorphous powder, or consist of thin, pale yellow or yellowish, transparent or translucent grains or scales. It should be capable of digesting not less than 3000 times its own weight of freshly coagulated and disintegrated egg-albumin. *Saccharated pepsin*, U. S. P., is a mixture of 10 parts of pepsin and 90 parts of sugar of milk.

Experiment 62. Use the U. S. P. process for the valuation of pepsin, as follows: Prepare, first, the following three solutions: A. To 294 c.c. of water add 6 c.c. of diluted hydrochloric acid. B. In 100 c.c. of solution A dissolve 0.067 gramme of the pepsin to be tested. C. To 95 c.c. of solution A, brought to a temperature of 40° C. (104° F.), add 5 c.c. of solution B. The resulting 100 c.c. of liquid will contain 0.21 gramme of HCl, 0.00335 gramme of pepsin, and 98 c.c. of water.

Keep an egg in boiling water for fifteen minutes; rub the coagulated albumin through a No. 30 wire sieve, place 10 grammes of this albumin in a 200 c.c.

flask, add solution C, shake well, and place the flask in a water-bath, or thermostat, kept at a temperature of 38° to 40° C. (100° to 104° F.) for six hours, and shake it gently every fifteen minutes. If, at the expiration of that time, the albumin should have disappeared, leaving at most only a few, thin, insoluble flakes, then the dissolving power of the pepsin examined is not less than 3000.

The relative proteolytic power of pepsin, stronger or weaker than that described above, may be determined by ascertaining, through repeated trials, how much of solution B made up to 100 c.c. with solution A will be required to dissolve 10 grammes of albumin under the conditions given above.

Pancreatin, U. S. P. This preparation is a mixture of the enzymes existing in the pancreas of warm-blooded animals, and is usually obtained from the fresh pancreas of the hog. It is a yellowish, or grayish, almost odorless powder, soluble in water, insoluble in alcohol. It has the power to digest proteids, and to convert starch into sugar.

If there be added to 100 c.c. of water contained in a flask, 0.28 gramme of pancreatin and 1.5 gramme of sodium bicarbonate, and afterward 400 c.c. of fresh cow's milk, previously heated to 38° C. (100° F.), and if this mixture be maintained at the same temperature for thirty minutes, the milk should be so completely peptonized that, if a small portion of it be transferred to a test-tube and mixed with some nitric acid, no coagulation should occur.

Gelatinoids. To this group belong a number of substances occurring in bones, skins, horns, hair, nails, feathers, etc., and having generally the property of forming a jelly with water. The organic matter in bones, usually called *ossein*, contains, besides an albuminous substance, the two gelatinoids *collagen* and *gelatin*, an impure mixture of which forms common glue.

QUESTIONS.—501. To which class of substances is the term proteids applied, and which elements enter into their composition? 502. By what processes are proteids formed in nature, and where do they occur? 503. State the general properties of proteids. 504. How are proteids acted upon by heat, nitric acid, and Millon's reagent? 505. Into which groups may proteids be classified, and how do they differ from each other? 506. Mention some native albumins; state where they are found, and by what tests they are characterized? 507. How may blood-fibrin be obtained and what are its properties? 508. State formation and characteristic properties of peptones. 509. What elements are found in hæmoglobin, where does it exist, and what are its characteristic properties? 510. What is pepsin, and how does it act upon proteids?

VII.

PHYSIOLOGICAL CHEMISTRY.

52. CHEMICAL CHANGES IN PLANTS AND ANIMALS.

General remarks. Physiological chemistry is that part of chemistry which has more especially for its object the various chemical changes which take place in the living organism of either plants or animals. It considers the chemical nature of the different substances used as "food," follows up the changes which this food undergoes during its absorption and assimilation in the organism, and treats, finally, of the products eliminated by it. The chemical changes taking place in the organism are either normal (in health) or abnormal (in disease). The abnormal products formed under abnormal conditions are generally termed "pathological" products.

Difference between vegetable and animal life. As a general rule, it may be stated that the chemical changes in a plant are *progressive* or *constructive*, in an animal *regressive* or *destructive*. That is to say, plants take up as food a small number of inorganic substances of a comparatively simple composition, convert them into organic substances of a more and more complicated composition with the simultaneous liberation of oxygen, whilst animals take up as food these organic vegetable substances of a complex composition, assimilating them in their system, where they are gradually used (burned up) and finally discharged as waste products, which are identical (or nearly so) with those substances serving as plant food.

Plant food.	*Waste products of animal life.*
Carbon dioxide.	Carbon dioxide.
Water.	Water.
Ammonia, NH_3.	Urea, $CO(NH_2)_2$.
Nitrates, $MxNO_3$.	Urates, $MxC_5H_2N_4O_3$.
$\left.\begin{array}{l}\text{Phosphates}\\\text{Sulphates}\\\text{Chlorides}\end{array}\right\}\text{ of }\left\{\begin{array}{l}\text{Calcium.}\\\text{Magnesium.}\\\text{Sodium.}\\\text{Potassium.}\end{array}\right.$	$\left.\begin{array}{l}\text{Phosphates}\\\text{Sulphates}\\\text{Chlorides}\end{array}\right\}\text{ of }\left\{\begin{array}{l}\text{Calcium.}\\\text{Magnesium.}\\\text{Sodium.}\\\text{Potassium.}\end{array}\right.$

Formation of organic substances by the plant. As shown in the preceding table, plants take up the necessary elements for organic matter from a comparatively small number of compounds. All carbon is derived from carbon dioxide; hydrogen chiefly from water; oxygen from either of the two substances named, as well as from the various salts; nitrogen either from ammonia, or from nitrates or nitrites; while sulphur and phosphorus are derived from sulphates and phosphates respectively. These substances are taken into the plant chiefly by the roots, the assimilation of the necessary mineral constituents being facilitated by an acid secretion (discharged from the roots) which has a tendency to render these salts, present in the soil and surrounding the roots, soluble.

Water having absorbed more or less of carbon dioxide, of ammonia or ammonium salts, and of nitrates, phosphates, and sulphates of potassium, calcium, etc., enters the plant through the roots by a simple process of diffusion, and is carried to the various green parts of the plant (chiefly to the leaves), where, under the influence of sunlight, a chemical decomposition and the formation of new compounds take place, the liberated oxygen being discharged directly through the leaves into the atmosphere.

It is difficult to explain fully the process of the formation of highly complex organic compounds in the plant, because we know so little in regard to the intermediate products which are formed. However, it is fair to assume that the various compounds above mentioned as plant food are first decomposed (with liberation of oxygen) in such a manner that residues or unsaturated radicals are formed, which combine together. From these compounds, produced at first, more complicated ones will be formed gradually by replacement of more hydrogen, oxygen, or other atoms by other residues.

The following equations, while not showing the various radicals and intermediate compounds formed, may illustrate some of the results obtained by the plant in forming organic compounds:

$$
\begin{aligned}
CO_2 + H_2O &= H_2CO_3 \\
& H_2CO_3 - O = H_2CO_2 = \text{Formic acid.} \\
2CO_2 + H_2O &= H_2C_2O_5 \\
& H_2C_2O_5 - O = H_2C_2O_4 = \text{Oxalic acid.} \\
6CO_2 + 6H_2O &= C_6H_{12}O_{18} \\
& C_6H_{12}O_{18} - 12O = C_6H_{12}O_6 = \text{Glucose.} \\
10CO_2 + 8H_2O &= C_{10}H_{16}O_{28} \\
& C_{10}H_{16}O_{28} - 28O = C_{10}H_{16} = \text{Oil of turpentine.} \\
10CO_2 + 4H_2O + 2NH_3 &= C_{10}H_{14}O_{24}N_2 \\
& C_{10}H_{14}O_{24}N_2 - 24O = C_{10}H_{14}N_2 = \text{Nicotine.}
\end{aligned}
$$

The above formulas show that the formation of organic compounds in the plant is always accompanied by the liberation of oxygen, and it may be stated, as a general rule, that no organic substance (produced in nature) contains a quantity of oxygen sufficient to convert all carbon into carbon dioxide and all hydrogen into water, which fact also explains the combustibility of all organic substances.

Why it is that the living plant has the power of forming organic substances in the manner above indicated, we know not, and we know very little even in regard to the means by which the living cell accomplishes this formation, but we do know that sunlight is that agent the action of which is indispensable for the plant in the formation of more complicated organic substances from simpler ones.

Decomposition of vegetable matter in the animal system. It has been stated above that the process of chemical decomposition taking place in the animal system is chiefly regressive or destructive, that is to say, the substances formed in the plant are taken into the animal system, where they are gradually oxidized by the inhaled atmospheric oxygen, thereby being converted into simpler forms of combination which are finally eliminated as waste products.

It has been shown above how a molecule of glucose which is formed in the plant requires not less than 6 molecules of carbon dioxide, and the same number of molecules of water for its formation, 6 molecules of oxygen being eliminated. A molecule of glucose taken into the animal system undergoes the reverse process; by combining there with 6 molecules of oxygen it is converted into 6 molecules of carbon dioxide and the same number of molecules of water, thus:

$$C_6H_{12}O_6 + 12O = 6CO_2 + 6H_2O.$$

Animal food. The food taken by animals is (beside water and a few of its mineral constituents) all derived from vegetables, but it is taken from them either directly or indirectly; in the latter case it has been taken previously into and assimilated by other animals, as in case of food taken in the form of meat, milk, eggs, etc. While some animals (herbivora) feed upon vegetable, and some (carnivora) upon animal food exclusively, others are capable of taking and assimilating either.

The fact that animal food is derived from vegetable matter, renders it superfluous to state that the elements taking an active part in the formation of either vegetable or animal matter are identical. Of the total number of 69 elements, only 14 are found as necessary constituents of the animal body. These elements are carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus, chlorine, fluorine, silicon, calcium, magnesium, sodium, potassium, and iron. A few other elements, such as aluminum, manganese, copper, etc., are sometimes found in the animal system, but they cannot be looked upon as normal or necessary constituents.

The various kinds of animal food are derived chiefly from three groups of organic substances, viz., carbohydrates (sugars, starch, etc.), fats, and albuminous or nitrogenous substances. The inorganic substances, such as phosphates, chlorides, etc., required by the animal in the construction of bones, for the liberation of hydrochloric acid in the gastric juice, etc., are generally found as constituents of various kinds of food or are derived from drinking-water. Milk contains all the necessary organic or inorganic constituents; bread is rich in phosphates, which latter are also found in smaller or larger quantities in nearly all kinds of vegetable and animal food.

Through the food are supplied those compounds which supply the constituents that replace the exhausted material of the living cells, and by chemical changes their inherent potential energy is converted into the heat of the body and into the kinetic energy used in working the living mechanism. Whilst the nitrogenous substances have primarily the task of continuously replacing the wear and tear of the nitrogenous tissues, they also serve to keep up the animal heat and consequently the involuntary or voluntary motion.

To some extent, the animal body may be regarded as a complicated machine, in which the potential energy, supplied by the food, is converted into actual energy of heat and mechanical labor. The main difference is that in our machines the fuel serves as the source of energy only, while in the body the food is mainly changed first into tissue (thus building up and renewing the body constantly), serving as fuel afterward. While in the best steam-engine only one-tenth of the fuel is utilized as mechanical work, over one-fifth of the energy of the food is realized in the human body.

The relative proportions in which the two kinds of food are taken by animals depend upon the nature of the animal and upon its particular condition of existence.

Below are given in column A the daily quantities of dry food required to maintain a grown person in good health, with neither loss nor gain in weight, while the figures in column B refer to the quantities of dry food for a working man of average height and weight.

	A.	B.
Proteids	100 grammes.	130 grammes.
Fats	100 "	85 "
Carbohydrates	240 "	400 "
Inorganic salts	25 "	30 "
Water	2600 "	2600 "

The table below shows that 900 grammes (about 2 pounds) of bread, 340 grammes ($\frac{3}{4}$ pound) of lean meat, and 57 grammes (2 ounces) of butter will supply the quantities of solid food required in a day by an active laborer:

	Bread (900 grammes).	Lean meat (340 grammes.)	Butter (57 grammes).	Bread, meat, and butter.
Proteids	74 grammes.	66 grammes.	...	140 grammes.
Fats	14 "	12 "	50 grammes.	76 "
Carbohydrates	460 "	...	...	460 "
Inorganic salts	22 "	17 "	...	39 "

In providing a diet, it must be borne in mind that the *digestibility* of a food is more a measure of its nutritive value than its elementary composition. Different foods show great differences in the rapidity and completeness with which they are absorbed. Thus eggs, fresh meat, white bread, and butter are absorbed and assimilated more readily than pork, rye bread, potatoes, green vegetables, and bacon.

The relative proportions of nitrogenous and non-nitrogenous matter in various kinds of food are shown in the following table:

	Nitrogenous.	Non-nitrogenous.		Nitrogenous.	Non-nitrogenous.
Sweet potatoes	1	17	Pork	1	3
Rice	1	12	Fat mutton	1	2.7
Carrots	1	11	Peas (dried)	1	2.5
Potatoes	1	10	White beans	1	2.3
Bread	1	5.0–6.8	Milk	1	2.2
Flour	1	5.0-6.5	Beef	1	1.7
Turnips	1	6	Cheese	1	0.7
Onions	1	6	Meat	1	0.5–1.5
Oatmeal	1	5.5	Veal	1	0.1
Cocoa	1	5	White of egg	1	0

Nutrition. In the process of nutrition five phases may be distinguished, viz.: *Digestion, absorption, assimilation, destructive metamorphosis,* and *elimination of waste products.*

Digestion is the process of converting food material into dialyzable compounds, or into other forms of matter capable of absorption. Absorption is the mechanical process of transferring the digested materials from the alimentary canal into the circulation. Assimilation includes the changes taking place after they are absorbed until they have become a part of living cells. Destructive metamorphosis includes those changes which take place chiefly in consequence of oxidation, the oxygen being supplied during the process of respiration. Elimination of waste products is the discharge of that material which is no longer needed in the system.

Digestion. It has been stated before that foods are divided into two classes, inorganic and organic, and that the latter are subdivided into albuminoids, carbohydrates, and fats. As a rule, the inorganic foods are taken into the body without chemical change. Before the organic foods can be absorbed, they have to undergo digestion. This is the process by which organic compounds, capable of acting as foods, are so altered that they may be absorbed.

The first part of the process of digestion is accomplished in the mouth and consists in the breaking up of the food by the teeth and mixing it with saliva, the process being known as *mastication*. In addition, the saliva, to a limited extent, converts starch into maltose. This action of the saliva is due to its ferment *ptyalin*. Other functions of the saliva are to keep the mucous membrane of the mouth moist and to lubricate the food bolus.

After being masticated, the food is passed into the stomach, where it comes in contact with the *gastric juice*. The active principles of the gastric juice are free hydrochloric acid, which is present in from 0.1 to 0.2 per cent., and the ferments pepsin and rennet. The proteids are the only compounds affected by the gastric juice. The free acid first converts them into *syntonin*, which is soluble in dilute acids, but is insoluble in water or solutions of neutral salts. The pepsin causes syntonin to take up water, converting it into *albumoses* and *peptones*, which latter, as stated in chapter 51, are dialyzable, and soluble in water, dilute acids, dilute alkalies, and neutral solutions. Rennet ferment has the power of coagulating milk in neutral solution—that is, of precipitating the casein. Starch cells and fat globules are set free by the gastric juice acting upon their albuminous envelopes.

After the food has been acted upon by the gastric juice it forms a very turbid mixture, *chyme*, which, by the contraction of the stomach, is forced through the pyloric orifice into the small intestine. Here it soon comes in contact with the *bile* and *pancreatic juice*.

The functions of the bile as a digestive fluid are: to assist in the emulsification of neutral fats; to promote the absorption of fats; by its diastatic ferment to convert starch and glycogen into sugar; to stimulate intestinal peristalsis; to assist in the evacuation of the feces, to which it furnishes the coloring matter; and, finally, to act as an intestinal antiseptic.

Pancreatic juice is alkaline in reaction and contains most likely four ferments, trypsin, steapsin, amylopsin, and one unnamed. Much the larger portion of fats are simply emulsified by the pancreatic juice. Under the influence of steapsin a small portion is broken up into fatty acids and glycerin. For example:

$$\underset{\text{Stearin.}}{C_3H_5.(C_{18}H_{35}O)_3O_3} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Stearic acid.}}{3C_{18}H_{36}O_2} + \underset{\text{Glycerin.}}{C_3H_5(OH)_3}.$$

A portion of the alkali present then unites with the fatty acid to form a dialyzable soap.

Amylopsin acts upon starches, converting them into maltose. The change is one of hydration :

$$\underset{\text{Starch.}}{2C_6H_{10}O_5} + H_2O = \underset{\text{Maltose.}}{C_{12}H_{22}O_{11}}.$$

Any albuminoids that may have escaped the action of the gastric juice are converted into peptones by trypsin. In this process, which is apparently one of hydration, the intermediate compound syntonin is not formed. The fourth, assumed and unnamed ferment of pancreatic juice, has the property of coagulating casein.

In addition to the above considered digestive fluids, there are the intestinal juices. They are, however, so small in quantity and so difficult of investigation that little is known of their action. They probably have properties similar to the pancreatic juice, though weaker than that secretion. By the combined action of the various digestive fluids, the chyme is gradually converted into *chyle*. It is a milky-white, or occasionally a yellowish fluid, having an alkaline reaction, a faint smell, a saltish taste, and a specific gravity varying from 1.007 to 1.022. It is this chyle which is absorbed by the intestinal villi, and forms the material from which the blood is constantly renewed.

Absorption. Assimilation. All forms of food that are dialyzable when taken into the stomach, or that are there converted into dialyzable compounds, are, for the most part, taken directly into the radicles of the portal vein by osmose. The products of intestinal digestion make their way partly into the bloodvessels and partly into the lacteals. It has been shown that the larger portion of fats which are not dialyzable get into the lacteals as fats, and not as dialyzable soaps. At present we do not understand the process by which this absorption of emulsified fats takes place.

All material absorbed by the lacteals is carried by the thoracic duct and poured into the left subclavian vein. All material taken up by the portal vein is first carried to the liver. In the liver the maltose undergoes dehydration, being thereby converted into an insoluble compound, isomeric with starch, and termed *glycogen*. This glycogen is stored up in the liver, and when wanted in the system is reconverted into soluble maltose.

Respiration. The most important changes in respired air are the changes in the quantities of oxygen and carbon dioxide. Pure air, after being dried, contains, by volume, of oxygen 20.8 per cent., of nitrogen 79.2 per cent., and a quantity of carbon dioxide (0.04 per cent.) so small that it need not be considered. When 100 volumes of air have been breathed once, it gains a little more than four parts of carbon dioxide and loses a little more than five parts of oxygen; so that the composition of 100 volumes of inspired air, when expired, is, after being dried, oxygen 15.4 parts, nitrogen 79.2 parts, and carbon dioxide 4.3 parts by volume.

Much the greater portion of the oxygen lost from respired air enters into combination with the hæmoglobin; a small portion is absorbed by the blood-serum. The immediate source of the carbon dioxide is the blood, in which it exists partly in simple solution and partly in a loose combination with some unknown body.

The blood is the common carrier of the body: from the alimentary canal it receives ultimately all the food material; from the lungs it receives oxygen; these it carries to the tissues for their sustenance; from the tissues it receives the products of destructive metamorphosis, and carries them to their proper organs of elimination.

The bright-red color of the arterial blood is due to oxyhæmoglobin. A large portion of this oxygen absorbed by the hæmoglobin is given up to the tissues as the blood passes through the capillaries, and we have then the reduced hæmoglobin to which is due the dark color of the venous blood.

In some way, not understood, the blood-plasma takes up the carbon dioxide from the tissues and carries it to the lung. It has been shown that the dark color of the venous blood is not due to the presence of carbon dioxide, but to a decrease of the oxygen.

In suspension in the plasma are found the food materials on their way to different portions of the body. A small percentage of peptones is found, but the quantity is so insignificant in proportion to the total amount absorbed, that it is extremely probable that they are converted into the more common forms of albumin.

Waste products of animal life. The changes which the food suffers after having been absorbed by the animal system are extremely complicated, and far from being thoroughly understood. Numerous products and organs are formed and nourished from and by the blood; among them muscular, nerve, and brain substance, excretions and secretions, such as milk, saliva, bile, gastric and pancreatic juice, etc., together with bones, teeth, hair, and many others.

Most of these substances (some excretions, such as milk and others, excepted) suffer a constant oxidation in the system, and are finally eliminated as waste products; in regard to the intermediate compounds formed in the tissues we know little, but it is highly probable that the reduction of the complicated food material to the simple forms of the waste products is very gradual. There are three channels through which the waste products are given off; they are the lungs, the skin, and the kidneys. By the lungs are eliminated chiefly carbon dioxide and some water, by the kidneys urine (which is a weak aqueous solution of urea, uric acid, urates, phosphates, chlorides, and sulphates of calcium, magnesium, sodium, potassium, etc.), and by the skin are constantly eliminated carbon dioxide and water, and during the process of sweating also more or less of the constituents of urine.

Chemical changes after death. After the death of either a plant or an animal, a chemical decomposition commences which finally results in the formation of those inorganic compounds from which the plant originally derived its food, viz., carbon dioxide, water, ammonia, sulphates, phosphates, etc. This decomposition of a dead body is generally a simultaneous fermentation or putrefaction, aided by decay or slow combustion.

There are numerous intermediate products formed, which differ according to the nature of the decomposing substance, or according to the conditions (degree of temperature, amount of moisture and air present, etc.) under which the decomposition takes place.

During the decomposition of dead vegetable matter (especially of moist wood) the intermediate products are frequently called *humus*, which substance (or better, mixture of substances) forms the chief part of the organic matter in the soil.

During the decomposition of dead animals, the sulphur is first eliminated as hydrogen sulphide, and a number of other intermediate products have been shown to be formed; among them certain organic

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QUESTIONS.—511. What is the difference between vegetable and animal life from a chemical point of view? 512. Mention the chief substances serving as plant food. 513. Explain the formation of organic substances in the plant. 514. What elements enter into the animal system as necessary constituents? 515. The members of which three groups of organic substances are chiefly used as food by animals? 516. Give a full explanation of respiration. 517. Explain bases called *ptomaines* or *cadaveric alkaloids*, substances which have been spoken of in Chapter 50. The decomposition of organic matter may be prevented under conditions which have been mentioned heretofore in connection with putrefaction.

53. ANIMAL FLUIDS AND TISSUES.

Constituents of the animal body. The animal body consists mainly of three kinds of matter, viz., water, organic and inorganic matter. It contains of water about 70 per cent., of organic matter 25 per cent., and of inorganic matter about 5 per cent. The water may be determined by drying a weighed quantity in an air-bath at a temperature of 100° to 105° C. (212° to 221° F.); the organic matter is estimated by burning the dried substance, and the inorganic matter (ash) by weighing the residue. Some of the elements which are left in the inorganic residue have, however, been actually constituents of organic compounds; iron, for instance, which is left in the ash, has been chiefly a constituent of hæmoglobin; sulphur, left as a sulphate, may have been a constituent of albumin, etc.

The relative quantities of the three constituents in some of the animal fluids and tissues is shown in the following table:

	Water.	Organic and volatile matter.	Inorganic residue (ash).
Saliva	99.50	0.32	0.18
Gastric juice	99 43	0.33	0.24
Pancreatic juice	90.97	8.18	0.85
Bile	85.92	13.30	0.78[1]
Chyle	91.80	7.40	0.80
Lymph	91 80	7.40	0.80
Pus	87.00	12.20	0.80
Cows' milk	87.00	12.25	0.75
Human milk	86.80	12.85	0.35
Blood	79.50	19.70	0.80
Blood corpuscles	54.60	44.68	0.72
Blood serum	90.50	8.68	0.82
Urine	95.70	3.00	1.30
Bone (varies widely)	22.00	26.00	52.00
Dentine	10.00	25.00	65.00
Enamel	0.40	3.60	96.00

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the chemical changes which food suffers during digestion. 518. Mention the principal fluids which are secreted by various organs of the animal body in order to facilitate or cause digestion. 519. What are the waste products of animal life, and through which channels are they eliminated? 520. What is the final result of the decomposition of dead plants or animals?

[1] The metals in combination with the biliary acids not included.

The complex nature of the various organic matters has been referred to in the preceding chapter, and will be more fully considered below; but it may be mentioned here, that some of these organic substances (or groups of substances) may be separated by a successive treatment of the animal matter with various solvents. Thus, by treating with ether or carbon disulphide, all fats may be extracted ; by then treating with alcohol and water successively other substances (generally termed *extractive matter* or *extractives*) are dissolved, which may be obtained by evaporating the solution.

Among the extractives are found kreatin and kreatinin, urea, uric acid, organic salts, etc. After the fatty matter and the extractives have been removed there remains an elastic and somewhat horny mass, which consists chiefly of proteids (albumin, fibrin, globulin, etc.).

The complete separation of all substances is extremely difficult on account of the great similarity in properties of many of these substances, and the rapid changes which they suffer when acted upon by solvents or chemical agents.

As the nature or composition of many of the inorganic salts present in the animal tissues is changed during the burning off of the organic matter, it is necessary to determine them either in the aqueous solution (extract) or by subjecting the animal matter to dialysis, by which process they may be more or less completely separated from the organic matter, which is left in the dialyzer, whilst the salts pass through the membrane.

Experiment 63. Cut a mouse (or some other small animal) into fragments weigh and place them in a weighed dish; expel all water by heating the dish first over a water-bath, and then in an air-bath at a temperature of about 110° C. (230° F.) until there is no longer any loss in weight; this loss is the amount of water present in the animal. Disintegrate the dry pieces further by grinding in a mortar and cutting with a pair of scissors, mix well and ignite a few grammes in a platinum crucible until all organic matter is burned off and a white or nearly white residue of inorganic matter is left. (Complete combustion is facilitated by cooling and heating alternately several times, since the animal charcoal, left after the first ignition, readily absorbs atmospheric oxygen, which aids in combustion when again heated.) From the results obtained by the ignition of the portion of dry animal matter calculate the organic and inorganic matter of the animal operated on.

Digest the inorganic residue with water, filter and test in the filtrate for chlorides by silver nitrate. Dissolve the residue upon the filter in dilute hydrochloric acid and test portions of this solution for phosphoric acid by means of ammonium molybdate; for iron by potassium ferrocyanide ; for sulphuric acid by barium chloride, and for calcium by adding an excess of sodium acetate and then ammonium oxalate.

Weigh a few grammes of the dried animal matter and digest it in a stoppered flask with about 10 parts of ether for an hour; filter, and repeat the operation once or twice; allow the ether to evaporate in a small dish, previously weighed; the residue left consists chiefly of fats, which may be recognized by their physical properties.

Digest the animal matter left from previous treatment twice with hot alcohol and twice with boiling water; evaporate the alcoholic and aqueous solutions separately; they contain the so-called extractives and soluble salts.

Dry the exhausted animal matter completely as before and weigh it; it consists chiefly of insoluble salts and albuminous substances. Ignite and burn as stated above. The loss represents mainly albuminoids. Notice the difference between the percentage of inorganic matter left now and in the determination made before; this difference represents the soluble inorganic compounds.

Blood. Two kinds of blood are distinguished, the arterial or oxidized and the venous or deoxidized blood. Arterial blood as it is present in the system, or immediately after it has been drawn from the body, is a red liquid of an alkaline reaction and a specific gravity of about 1055. Upon examination under the microscope, blood is seen to consist of a colorless fluid, called *plasma* or *serum*, in which float small globules or *corpuscles* which make up about 40 per cent. of the whole volume of blood. These corpuscles are of three varieties, viz.: red and white corpuscles, and blood plates. The red corpuscles, which give to the blood its red color, are biconcave discs, about $\frac{1}{3200}$ of an inch in diameter; the white corpuscles are simple cells, and somewhat larger than the red corpuscles; they are present in the proportion of about 1 to 350 of red. More recently have been discovered "blood plates," pale, colorless, oval, round or lenticular discs which vary in size.

The composition of normal human blood is about as follows:

Water	79.50	per cent.
Serum-albumin	7.34	"
Fibrin	0.21	"
Hæmoglobin	11.64	"
Fatty matters	0.18	"
Extractives	0.32	"
Ash	0.81	"

Wet red blood-corpuscles contain of water 54.63 per cent., hæmoglobin 41.1 per cent., other proteids 3.9 per cent., fats (chiefly cholesterin and lecithin) 0.37 per cent. The quantity of water in corpuscles varies widely, and most likely ranges in healthy blood from 76 to 80 per cent. Dried corpuscles contain of hæmoglobin about 90 per cent.

The white blood-corpuscle consists of a thin envelope filled with an albuminoid (or a mixture of them) called protoplasm.

The blood-plasma is a colorless liquid of the average composition as follows:

	Per cent.
Water	90.20
Albumin	5.30
Fibrinoplastin	2.20
Fibrinogen	0.30
Fatty matters	0.25
Crystallizable nitrogenous matter	0.40
Other organic ingredients	0.50
Mineral salts	0.85

The alkaline reaction of blood is due to the presence of acid sodium carbonate, $NaHCO_3$, and sodium phosphate, Na_2HPO_4, both of which have a weak alkaline reaction. Besides these alkaline salts, blood also contains others, among them chiefly sodium chloride, and also the chlorides, phosphates, and sulphates of calcium, magnesium, sodium, potassium, etc.

When blood leaves the body and is allowed to stand a while (or, quicker, on shaking or agitating it violently) it separates into a semi-solid mass termed *clot*, and a pale-yellow liquid termed *serum*, which latter, however, also solidifies after a time in consequence of the coagulation of the serum-albumin. Clot consists of fibrin, holding in its meshes the blood corpuscles; the latter may be removed by washing the clot in a stream of water. Another method for obtaining the corpuscles is to dilute mammalian blood with 10 volumes of a 2 per cent. sodium chloride solution, which prevents coagulation, but allows the corpuscles to settle at the bottom of the fluid.

Fibrin is a proteid, which exists not as such in the blood, but forms whenever the latter is taken from the body (or under some circumstances when within the living body). It is now assumed, that for the formation of fibrin four factors are necessary, viz., fibrinoplastin, fibrinogen, fibrin ferment, and a small portion of neutral salts. The origin of the fibrin ferment is not positively known, but it is supposed to come from the edges of the wounded bloodvessels. The other factors are all present in the blood. How these substances by their interaction produce fibrin is not known; fibrinogen is the only one of which the total quantity is used. There is always an excess of fibrino-plastin. While the presence of fibrin ferment and neutral salts is necessary, their quantities do not seem to be diminished. The blood corpuscles take no active part in the formation of the clot, but are simply entangled in its meshes.

Hæmoglobin is the chief constituent of the red corpuscles, and the substance which carries oxygen to the various tissues, as described in connection with the consideration of the process of respiration in the previous chapter.

Experiment 64. Pour some freshly drawn venous blood into four volumes of a saturated solution of sodium sulphate contained in a vessel which stands in ice; mix and set aside for several hours; no coagulation occurs and the corpuscles settle to the bottom of the vessel. Pour off the supernatant liquid, collect the sediment on a filter, and wash it first with cold solution of sodium sulphate and then with water.

Prepare hæmoglobin from these corpuscles as follows: agitate the collected mass violently with small quantities of ether until the corpuscles are nearly dissolved; allow the liquid to settle, filter, render the filtrate slightly acid with acetic acid, and add alcohol as long as the precipitate first formed continues to dissolve; cool the red solution to 0° C. (32° F.) for several hours, when crystals of hæmoglobin will form; collect these on a filter and wash with an ice-cold mixture of alcohol and water.

Examination of blood-stains. Blood-stains may be recognized, after having been washed off with as little water as possible, by the following methods:

1. Examine the reddish fluid under the microscope for blood corpuscles.

2. Evaporate a drop of the fluid on a microscope slide with a minute fragment of sodium chloride, cover with a cover-glass, allow a drop of glacial acetic acid to enter from the side and warm gently; abundant crops of hæmin crystals are seen under the microscope after cooling.

3. Add a drop of the fluid to some freshly prepared tincture of guaiacum in a test-tube and float on the surface of an ethereal solution of hydrogen dioxide; a blue ring forms at the junction of the ethereal solution and the guaiacum. (Blood is, however, not the only substance showing this reaction.

4. The spectroscope shows bands characteristic of hæmoglobin.

Chyle is a white, creamy liquid, of a strongly alkaline reaction, having in common with blood the property of coagulating (upon leaving the organism) into white fibrin and turbid serum. The composition of chyle differs according to the state of digestion; it contains:

	During full digestion.	During fasting.
Water	91.8 per cent.	96.80 per cent.
Fibrin	0.2 "	0.09 "
Proteids	3.5 "	2.30 "
Fats	3.3 "	0.04 "
Extractives	0.4 "	0.28 "
Salts	0.8 "	0.49 "

Lymph is a clear, colorless, or slightly yellow liquid of a faint alkaline reaction; in composition it closely resembles chyle, but differs from it in containing smaller quantities of fibrin and fatty matters.

Saliva is secreted by several glands situated in the mouth, and represents in its mixed condition a viscid, generally slightly alkaline, tasteless, inodorous liquid of a specific gravity of 1.002 to 1.008. It contains of

Water	99.49	per cent.
Ptyalin	0.12	"
Epithelium and mucin	0.13	"
Fatty matters	0.11	"
Salts	0.15	"

Ptyalin, the active principle of saliva, is a ferment which has the power of converting starch into maltose and small quantities of dextrose. Intermediary between the starch and sugar are two products known as *erythrodextrin* and *achroödextrin.* Starch is recognized by a deep blue color produced by a solution of iodine and potassium iodide in water. Erythrodextrin gives a mahogany brown or violet color, and achroödextrin, maltose or dextrose do not color the iodine solution at all. The composition of ptyalin is doubtful. Among the various salts of saliva is found potassium sulphocyanate, as may be shown by the addition of a drop of ferric chloride solution, which produces a deep red color, disappearing on the addition of mercuric chloride (difference from meconic acid).

Experiment 65. To a few c.c. of thin starch paste add an equal volume of saliva, mix well and digest at a temperature of 35°–40° C. (95°–104° F.) for about half an hour. Examine the liquid for sugar by Fehling's solution.

Gastric juice is a liquid secreted by the follicles of the stomach. It can be obtained, in a fairly normal condition, either from animals (dogs) or from man, by the aid either of gastric fistulæ, or of the stomach-pump. It is a thin, nearly colorless liquid, having a somewhat sour taste, an acid reaction, and a specific gravity varying from 1.004 to 1.010. The total solids are generally less than 1 per cent., nearly one-half being inorganic salts, chiefly the chlorides and phosphates of alkali and alkaline earth metals. The organic matter present, and amounting to about 0.3 per cent., is chiefly pepsin and a little mucin.

Organic acids, chiefly lactic and butyric, are frequently found in the stomach, but these are not secreted in the gastric juice itself, but are produced by some fermentative action from the food after it has entered the stomach. The acidity of gastric juice itself is due to free hydrochloric acid, present in quantities varying from 0.1 to 0.3, or even 0.4 per cent.

The nature of the decomposition resulting in the liberation of free hydrochloric acid is not known, but it may possibly be formed by the action of sodium phosphate on calcium chloride:

$$\underset{\substack{\text{Sodium}\\\text{phosphate.}}}{2(Na_2HPO_4)} + \underset{\substack{\text{Calcium}\\\text{chloride.}}}{3CaCl_2} = \underset{\substack{\text{Calcium}\\\text{phosphate.}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{Sodium}\\\text{chloride.}}}{4NaCl} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl.}$$

According to others, the hydrochloric acid is liberated by the action of acid sodium carbonate on sodium chloride:

$$\underset{\substack{\text{Sodium acid}\\\text{carbonate.}}}{NaHCO_3} + \underset{\substack{\text{Sodium}\\\text{chloride.}}}{NaCl} = \underset{\substack{\text{Sodium}\\\text{carbonate.}}}{Na_2CO_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{HCl.}$$

The above formulas show the reverse action of that which these substances exert upon each other under common conditions, but it must be remembered that the living cell is capable of decomposing matter generally in a manner different from that which it suffers ordinarily.

The average composition of pure gastric juice may be approximately stated thus:

Water	99.26	per cent.
Pepsin and other organic matter	0.30	"
Rennet	?	"
Free hydrochloric acid	0.22	"
Alkali chlorides	0.20	"
Phosphates of calcium, magnesium, and iron	0.02	"

Pepsin, besides hydrochloric acid, the most important constituent of gastric juice, has been spoken of heretofore; it has, in the presence of free hydrochloric acid, the power of converting proteids into albumoses, and finally into peptones. Pepsin is not secreted by the gastric tubules as such, but in a preliminary stage or pro-enzyme (pepsinogen), and is changed by the hydrochloric acid into pepsin.

Another ferment, known as rennet, is found in the gastric secretion. Like pepsin, it is secreted in a preliminary stage or pro-enzyme (rennet zymogen). Rennet has the power of coagulating milk in neutral solutions, that is, of precipitating the casein.

Experiment 66. Open the stomach of a pig, sheep, or calf, recently killed while fasting; wash it rapidly in cold water, spread it out and scrape off the mucous surface; digest it under frequent stirring with about ten parts of water for six hours, and filter. The solution contains pepsin—which verify by its dissolving action on coagulated albumin.

The solution may also be evaporated to dryness with or without sugar at a temperature not exceeding 40° C. (104° F.), and the dry pepsin tested by the directions given in Experiment 62.

Clinical examination of gastric juice. The chemical examination of gastric juice, or of contents of stomach, is now considered of great importance in the diagnosis of diseases of the stomach. The juice for examination is obtained as follows: On an empty stomach, the patient partakes of a test-meal, consisting usually of bread and water, and an hour after or later (depending upon the form of meal administered), the contents of the meal are withdrawn by means of a stomach-tube. The liquid is filtered and used for further examinations. These examinations consist of the following determinations: *a.* Reaction; *b.* presence of free acids; *c.* presence of free hydrochloric acid; *d.* presence of lactic and other organic acids; *e.* total acidity; *f.* estimation of free hydrochloric acid; *g.* presence of pepsin and pepsinogen; *h.* presence of rennet ferment and rennet zymogen; *i.* detection of proteids; *j.* detection of carbohydrates.

a. Reaction. This should be, and in all normal juices is, distinctly acid to litmus paper.

b. Free acids. The presence of free acids is detected by congo-paper. This paper is prepared by soaking unsized paper in a 1 per cent. aqueous solution of congo-red, and drying. If a drop of juice is placed upon the paper, the presence of free acids is indicated by the change of color from red to blue; if the blue color is intense, free hydrochloric acid is present. (Acid salts, such as acid phosphates, do not act on congo-red.)

c. Free hydrochloric acid. There are a number of reagents for the detection of free hydrochloric acid. The more important of these are: methyl-violet, tropæolin 0 0, phloroglucin-vanillin, and resorcin.

Methyl-violet. If a concentrated aqueous solution of methyl-violet is prepared and added to gastric juice containing free hydrochloric acid, a change from violet to blue is at once noted.

Tropæolin 0 0. Dissolved in alcohol the brownish-yellow solution of tropæolin 0 0 (diphenylamine-orange) is changed to a brown-red or deep-red color upon the addition of juice containing free hydrochloric acid. The same reaction may be made with filter-paper, soaked for some time in an alcoholic solution of the reagent, allowed to dry, and used as test-paper. Hydrochloric acid turns this paper brown, and upon heating the brown color changes to blue. (The paper does not keep unchanged over a month.)

Phloroglucin-vanillin. This reagent is made by dissolving 2 parts of phloroglucin and 1 part of vanillin in 30 parts of alcohol. It is a very sensitive and reliable reagent for the detection of free hydrochloric acid. Five drops of the solution mixed with an equal quantity of gastric filtrate are gently heated over a Bunsen flame. On complete evaporation a distinct red color or tinge appears in the presence of not less than 0.01 per cent. of hydrochloric acid. The formation of cherry-red crystals indicates the presence of large quantities of the acid. Organic acids have no action on this reagent.

Resorcin. This reagent is equally as sensitive as, and more stable than, phloroglucin-vanillin. The solution is obtained by dissolving 5 parts of resublimed resorcin and 3 parts of cane-sugar in 100 parts of dilute alcohol. The manner of testing with this reagent is the same as described above for phloroglucin-vanillin; a bright-red tinge or color appears, even when very small quantities of free hydrochloric acid are present.

d. Lactic acid. Uffelmann's reagent answers best for detecting this acid. It is made by adding 1 or 2 drops of ferric chloride solution to 10 c.c. of a 1 per cent. carbolic acid solution, and diluting this solution with water until it assumes an amethyst-blue color. To 2 c.c. of this solution an equal volume of gastric-juice is added. In the presence of at least 0.01 per cent. of lactic acid the liquid assumes a pure yellow color. As the presence of too much hydrochloric acid (or even of some other substances) prevents the change, it is well to shake (in doubtful cases) 10 c.c. of juice with 50 c.c. of ether, evaporating the ethereal solution to dryness, dissolving the residue in a few drops of water, and adding to this solution, which contains the lactic acid, the above reagent.

Butyric acid changes Uffelmann's reagent to brownish-yellow. Butyric and acetic acid may both be recognized by their odor.

e Total acidity. This is best determined by titration with an alkali; the estimation is conducted as follows: To 10 c.c. of the filtered liquid a few drops of phenol-phtalein solution are added, and to the mixture deci-normal potassium hydroxide solution is slowly added from a burette until the liquid assumes a slight reddish tint, which does not disappear on stirring.

It is customary to express the acidity in percentages, according to the quantity of deci-normal potassium hydroxide used. Thus, 52 per cent. acidity would indicate that every 100 c.c. of gastric filtrate are exactly neutralized by 52 c.c. of deci-normal potassium hydroxide.

Though the total acidity is due to a mixture of hydrochloric acid, organic acids, and acid salts, it is frequently expressed as hydrochloric acid. As 1 c.c. of deci-normal alkali solution corresponds to 0.003637 gramme of HCl, the number of c.c. of alkali used multiplied by the factor stated, gives the grammes of HCl in the 10 c.c. of juice used. Suppose 5.2 c.c. of alkali were required; this would correspond to 5.2 × 0.003637, equal to 0.0189 gramme of HCl in 10 c.c., or to 0.189 per cent.

f. Quantitative determination of free hydrochloric acid. There are numerous methods for the determination of the free hydrochloric acid of the gastric juice. The more important are as follows:

Determination by means of congo-red. An aqueous solution of congo-red has a bright-red color, which is changed to blue by free acids and restored to red by alkalies. Acid salts, such as acid phosphates, have no effect on this indicator. If, therefore, a titration of 10 c.c. of filtered gastric juice, to which enough of congo-red solution has been added to impart a distinct blue color, is made (as above described for total acidity) then the number of c.c. of deci-normal potassium hydroxide solution used to restore the red color indicates the quantity of free acid present. The calculation for hydrochloric acid is made as above mentioned. This method gives not only the quantity of free hydrochloric acid, but also of free organic acids. However, the very small quantities of organic acids which are usually present in the gastric filtrate after a trial breakfast do not materially vitiate the results. If larger quantities of organic acids are present, they must first be removed by shaking 10 c.c. of gastric juice with 100 c.c. of ether, in which these acids are soluble. The remaining acidity is due to free hydrochloric acid.

Determination by means of phloroglucin-vanillin. To 10 c.c. of gastric filtrate, deci-normal potassium hydroxide solution is added until no more free hydrochloric acid is indicated by testing a few drops of the liquid with phloroglucin-vanillin. If, for instance, no reaction occurs after having added 1.3 c.c. of potassium hydroxide solution, while a positive reaction was yet obtained with 1.2 c.c. of alkali solution, then we may say that 1.25 c.c. of deci-normal alkali solution were required for neutralization of 10 c.c. of gastric juice, or 12.5 c.c. alkali for 100 c.c. of juice. Multiplying 12.5 by 0.003637 (the factor for hydrochloric acid) we find 0.045 per cent. of hydrochloric acid as the result of the determination.

In place of phloroglucin-vanillin, the resorcin-sugar reagent, mentioned before, can be used with equal advantage as an indicator in the above titration.

Leo's method. This is employed for very accurate determinations of hydrochloric acid. It is based upon the principle that free acids are fully neutralized by the addition of calcium carbonate even at the ordinary temperature, while solutions of acid phosphates or of other acid salts retain their acidity.

To 10 c.c. of gastric filtrate are added 5 c.c. of concentrated solution of calcium chloride and a few drops of phenol-phtalein; titration is made with deci-normal potassium hydroxide (result A). To 15 c.c. of a second portion of gastric filtrate is added 1 gramme of pure, powdered calcium carbonate; the mixture is well shaken and filtered through a dry filter. Ten c.c. of this filtrate are removed, and air is passed through it in order to remove all carbon dioxide, which interferes with the use of phenol-phtalein as an indicator. (A double-bulbed syringe, to one end of which a piece of glass tubing is attached, answers well for this purpose.) Having added to the filtrate freed from carbon dioxide 5 c.c. of calcium chloride solution and phenol-phtalein, the titration is made (result B). As titration A gives the total acidity, titration B the acidity due to acid salts, therefore, A–B equal the alkali used for neutralizing the free acids. If fatty and lactic acids are not present the result indicates hydrochloric acid. Should these acids be present, they must first be removed—the fatty acids by distillation, the lactic acid by agitation with ether.

g. Pepsin and pepsinogen. In case free acid is present, 10 c.c. of gastric juice are placed in a beaker, and a small bit of dried fibrin, or a lamella of blood albumin (Merck), is added, and the beaker placed in a thermostat at a constant temperature of 38° to 40° C. (100° to 104° F.). Pepsin is indicated by the rapid solution of the flake of albumin. If free hydrochloric is absent, the juice is rendered acid with a drop of this acid and then tested in the manner described.

h. Rennet ferment and rennet zymogen. Rennet is tested for as follows: Ten c.c. of gastric juice are exactly neutralized with deci-normal alkali and mixed with an equal volume of neutral unboiled, or better boiled, milk. The mixture is placed in a thermostat at 38° C. (100° F.). If a casein coagulum is formed in ten to fifteen minutes, the coagulation is due to the rennet ferment.

Rennet zymogen is detected thus: Ten c.c. of gastric juice are rendered feebly alkaline and mixed with 2 c.c. of a 1 per cent. solution of calcium chloride and 10 c.c. of milk. If the rennet zymogen be present, a heavy cake of casein is precipitated in a few minutes.

i. Detection of proteids. Of these, syntonin, albumoses, and peptones are to be looked for. *Syntonin:* The gastric filtrate is exactly neutralized, whereupon a cloudiness or precipitate is formed, which is soluble both in alkalies and in acids. *Albumoses:* These are precipitated by a saturated solution of ammonium sulphate, while peptones remain in solution. *Peptones:* These are recognized by the biuret-test. The juice is rendered strongly alkaline with potassium hydroxide and a few drops of a cupric sulphate solution (1 in 1000) are added. A red color indicates the presence of peptones.

In the gastric contents, an hour after an ordinary test-meal, there is usually a large quantity of albumoses and a smaller amount of peptone. A large quantity of syntonin and a weak biuret reaction indicate a weakened proteid digestion and, therefore, a lessened secretion of pepsin and hydrochloric acid.

j. Detection of carbohydrates. Starch is recognized by the blue color produced by iodine solution (1 iodine, 2 potassium iodide, 100 water). The reaction is less marked in proportion to the amount of starch converted into dextrin and sugar.

Erythrodextrin gives a mahogany-brown color, and *achroödextrin* remains unchanged by the iodine solution. In strongly acid gastric contents erythrodextrin is found, while in cases in which hydrochloric acid is absent achroödextrin is almost exclusively present. In as much as sugar is present in the test-meal itself, it is useless to test for this substance.

Bile, secreted by the liver, is a thin, transparent liquid of a golden-yellow color, and a specific gravity of 1.020; it has a very bitter taste and an alkaline reaction; it varies widely in composition, the total solids ranging from 9 to 17 per cent., being always highest after a meal; its composition, moreover, is highly complex; the following is an average of five analyses of bile from subjects with healthy livers:

Water	91.68	per cent.
Mucus pigment	1.29	"
Taurocholate of sodium	0.87	"
Glycocholate of sodium	3.03	"
Fat	0.73	"
Soaps	1.39	"
Cholesterin	0 35	"
Lecithin	0 53	"

Bile obtained after death is of a brownish-yellow color; freed from mucus it will remain undecomposed for an almost indefinite period. The mucus may be separated by the addition of diluted alcohol and subsequent filtration.

The quantity of bile discharged daily by a grown person may be put at forty ounces, but a considerable quantity of this discharged bile is reabsorbed in a changed form by the intestines; only a small amount of bile matters (in a decomposed state, however) is discharged by the feces.

The functions of bile have been stated in the previous chapter.

Biliary pigments. Of these four are known, but it is probable that more exist. *Bilirubin*, $C_{16}H_{18}N_2O_3$, is, when amorphous, an orange-yellow powder; when crystalline, it forms red prisms. It is sparingly soluble in water, alcohol, and ether, readily soluble in hot chloroform and carbon disulphide. When treated with a mixture of concentrated nitric acid and sulphuric acid it turns first green, then blue, violet, red, and finally yellow. This reaction, known as *Gmelin's test*, is used for the detection of bile-pigments in urine and other fluids. (See Plate VIII., 7.)

Biliverdin, $C_{32}H_{36}N_4O_8$, is a green powder existing in green biles; it responds to Gmelin's test.

Biliary acids. *Glycocholic acid*, $C_{26}H_{43}NO_6$, and *taurocholic acid*, $C_{26}H_{45}NO_7S$, exist as sodium salts in the bile of man and most animals. Both salts may be obtained as colorless crystals, which dissolve in water, forming solutions of an acid reaction and an intensely bitter taste. Both acids are easily decomposed by heating with alkalies or with dilute acids, also by the action of putrefying material or by the chemical changes taking place in the intestines. In all these cases is formed *cholic acid*, $C_{24}H_{40}O_5$, and a second product, which in the case of glycocholic acid is *glycocol*, $C_2H_5NO_2$, and in the case of taurocholic acid *taurine*, $C_2H_7NO_3S$.

Pettenkofer's test. The biliary acids and their salts show a characteristic reaction known as Pettenkofer's test. This reaction is shown by adding very little cane-sugar to the liquid substance under examination, and adding concentrated sulphuric acid in such a manner that the temperature does not rise above 70° C. (158° F.). In the presence of biliary acids a beautiful cherry-red color is developed, which gradually changes to dark reddish-purple. (See Plate VIII., 8.)

The bile acids are, however, not the only substances which show the above reaction, and, therefore, it becomes in many cases necessary to separate the bile acids from other organic matter. This separation is accomplished by evaporating the substance under examination (urine, for instance), after having been mixed with a small quantity of coarse animal charcoal, to dryness at

100° C. (212° F.). The residue is extracted with absolute alcohol, the filtered alcoholic solution is again partially evaporated, and mixed with 10 volumes of absolute ether. The biliary acids are soluble in alcohol, but not in ether, or in ether containing one-tenth of alcohol. After standing an hour or two the biliary acids will form a deposit, which is collected on a small filter, dissolved in a little water, and mixed with a few drops of a strong solution of sugar. Upon the addition of sulphuric acid, with the precaution above mentioned, the characteristic colors will indicate the presence of the bile acids.

Experiment 67. Evaporate ox-bile to a thick syrup, digest it with 5 parts of pure, cold alcohol for two hours, and filter. Mix the filtrate, which contains sodium glycocholate and taurocholate, with freshly prepared animal charcoal, boil and filter; evaporate to dryness in a water-bath, redissolve in the smallest possible amount of pure alcohol, and add ether until the solution becomes markedly turbid. A white, crystalline mass is deposited in a few hours or days; this is known as *Plattner's crystallized bile*, and is a mixture of the two sodium salts mentioned.

Dissolve the mass in a small volume of water, adding a little ether and then dilute sulphuric acid; glycocholic acid crystallizes out in shining needles.

Cholesterin, $C_{26}H_{43}.OH$. This substance has been classed by physiologists among the fats, because it is greasy and soluble in ether, but its chemical constitution is that of an alcohol. It is found chiefly in bile, but also in blood, nerve-tissue, brain, contents of the intestines, feces, etc.; its presence in certain vegetables, as peas, beans, etc., has also been demonstrated.

Cholesterin crystallizes in colorless, silky needles, which are insoluble in water, alkalies, and dilute acids, but soluble in ether. It sometimes forms in the organism solid masses, known as *biliary calculi* or *gall-stones*, some of which are almost pure cholesterin.

Tests for cholesterin:

1. Evaporated with nitric acid it gives a yellow mass, which turns brick-red on addition of ammonia.
2. Mixed in the dry state with strong sulphuric acid, it produces a blue-red or violet color on addition of chloroform, the color changing to green on exposure to air.
3. Evaporated with a mixture of 2 volumes of sulphuric acid and 1 volume of ferric chloride solution, it turns violet.

Lecithins, $C_{44}H_{90}NPO_9$ or $C_{42}H_{84}NPO_9$. *Lecithin*, one of the constituents of bile, is a member of the group of substances generally termed *phosphorized fats* or *lecithins*. These bodies are highly complex in composition, and may be looked upon as fats formed from glycerin, in which hydrogen atoms are replaced by the radicals of phosphoric and fatty acids.

Pancreatic juice. There is no thoroughly reliable analysis of this highly complex liquid on record. It contains from 3 to 6 per cent. of solids, two-thirds of which are of organic, one-third of inorganic nature. Among the organic constituents are a number (certainly two, probably four) of enzymes: 1. *Amylopsin* converts starch into sugar (this action is more energetic than that of ptyalin); 2. *Trypsin* converts proteids into peptones (this action takes place in alkaline, but not in acid solution, as in case of pepsin; 3. *Steapsin* decomposes fats into glycerin and fatty acids; 4. An enzyme of which little is known, capable of emulsifying neutral fats.

Feces consist of that portion of the food which has not been taken into the system by absorption, and is discharged from the body mixed with some of the products of the biliary and intestinal secretions. The odor depends largely on two substances, *indol* and *skatol*, and to a less degree on the valerianic and butyric acids and the hydrogen sulphide present. Indol, C_8H_7N, belongs to the aromatic compounds, and is one of the products of the putrefaction of albumin. The quantity of feces passed depends on the nature of the food taken and on the energy of the digestive powers. A grown person, in normal condition, discharges from 7 to 9 ounces daily. An approximate analysis of the feces of a healthy adult shows:

Water	77.3	per cent.
Mucin	2.3	"
Proteids	5.4	"
Extractives	1.8	"
Fats	1.5	"
Salts	1.8	"
Resinous, biliary, and coloring matters	5.2	"
Insoluble residue of food	4.7	"

Bone is chemically distinguished from other tissues by the large quantity of inorganic salts which it contains. Dried bones contain about 31 per cent. of organic matter combined with 69 per cent. of mineral matter. Different bones (and even different parts of the same bone) of the same person differ somewhat in composition; moreover, the bones of a child contain somewhat more of organic matter than those of a grown person, as may be shown by the following analyses of the corresponding bone in children and a grown person:

	Child one year.	Child five years.	Man twenty-five years.
Organic matter,	43.42 per cent.	32.29 per cent.	31.17 per cent.
Tricalcium phosphate,	48.55 "	59.74 "	58.95 "
Magnesium phosphate,	1.00 "	1.34 "	1.30 "
Calcium carbonate,	5.79 "	6.00 "	7.08 "
Soluble salts,	1.24 "	0.63 "	1.50 "

Frequently human bones contain calcium fluoride, which substance, to the amount of 1 to 2 per cent., is a normal constituent of the bones of many animals. The organic matter of bone is called *ossein*, and is a mixture of collagen, elastin, and an albuminoid existing in the bone-cells. *Collagen* is a nitrogenous substance, insoluble in water, but forming when treated with it under the influence of heat and pressure, *gelatin*, an amorphous, tasteless, translucent substance, which swells up in boiling water, forming on cooling a soft jelly; an impure form of gelatin is common glue.

Teeth consist of three distinct tissues, viz., *dentine*, forming the chief mass, in its interior being the pulp cavity; *enamel*, investing the crown and extending some distance down the neck; and *cement*, covering the fangs. The composition of *cement* is almost the same as that of bone, its organic and inorganic constituents having the relative proportions of 30 : 70.

Dentine contains less water than bone and is also poorer in organic matter. The following table gives the composition of the dentine of an adult woman and man respectively:

	Woman.	Man.
Organic matter—ossein and vessels	27.61	20.42
Calcium phosphate	66.72	67.54
Calcium carbonate	3.36	7.97
Magnesium phosphate	1.08	2.49
Soluble salts, chiefly sodium chloride	0.83	1.00
Fat	0.40	0.58

Enamel is distinguished by the very small proportion of water and organic matter contained in it. Its average composition may be thus stated:

Water and organic matter	3.6
Calcium phosphate and traces of fluoride	86.9
Magnesium phosphate	1.5
Calcium carbonate	8.0

Tartar is the name given to the substance which deposits from alkaline saliva on the teeth. It is of a grayish, yellowish, or brownish color, and consists chiefly of calcium phosphate, with a little carbonate, but contains also some organic matter, salts of the alkalies, and silica.

Hair, nails, horns, hoofs, feathers, epithelium are nearly identical in composition. They all contain a nitrogenous substance, termed *keratin*, which is probably not a distinct chemical compound, but a mixture of several substances similar in composition and properties.

Mucus is secreted by the various mucous membranes, and is found in saliva, bile, connective tissues, feces, urine, etc. When pure it forms a clear, translucent or viscid mass; it contains a substance termed *mucin*, which swells up in water, and readily dissolves in water containing an alkali; from these solutions it is precipitated by acetic acid.

Muscles contain fibrin, albumin, myosin, kreatin, $C_4H_9N_3O_2$, sarkin, $C_5H_4N_4O$, xanthin, $C_5H_4N_4O_2$, uric acid, glucose, inosite, lactates, and salts.

Kreatin, sarkin, and xanthin are substances formed in the organism by oxidation of proteids, and may be looked upon as compound ureas or substances formed as intermediate products of the final conversion of proteids into urea, carbon dioxide, water, etc. These substances may indeed be decomposed artificially in such a manner that urea is produced as one of the products of decomposition.

Brain consists of so many individual parts that the analysis of it as a whole is of little value, and to separate these parts successfully is a task not yet accomplished. Brain, as a whole, contains cerebrin, lecithin, cholesterin, protagon, and many other substances, some of which are distinguished by the large quantity of phosphorus they contain.

54. MILK.

Properties and composition. Milk is the secretion of the mammary glands, the presence of which is characteristic of the class of

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QUESTIONS.—521. What three kinds of matter are found as constituents of the animal body, and how can they be determined quantitatively? 522. Mention the chief constituents of blood, and state those which predominate in serum and in the corpuscles respectively. 523. What substances cause the clotting of blood, and what explanation can be given? 524. How may blood-stains be recognized? 525. What is the active principle of saliva, and how does it act on starch? 526. State the composition of gastric juice, and explain its physiological action. 527. State the general properties of bile, and mention its chief constituents. 528. Give Gmelin's test for biliary pigments, and Pettenkofer's test for biliary acids. What precautions are necessary in using the latter test? 529. What is cholesterin? State its properties and reactions. 530. Mention the principal constituents of muscles, bone, teeth, and hair.

animals known as mammalia. The milk of different animals differs somewhat in composition, but it always contains all the constituents necessary for a normal development of the various tissues, liquids, organs, etc., of the young mammal, which generally feeds exclusively upon milk for a shorter or longer period of its early life.

Milk is an opaque, aqueous solution of casein, albumin, lactose, and inorganic salts, holding in suspension small globules of fat, invested, most likely, with coatings of casein or with some other albuminous envelope. The reaction of woman's milk and that of the herbivora is normally alkaline, but that of carnivora is acid. Its specific gravity ranges from 1.029 to 1.033, but may in extreme cases vary between 1.018 and 1.045.

The average composition of various kinds of milk is given below, but it must be remembered that milk not only differs in certain species, but also in the same animal at different times; for instance, the quality and quantity of food taken, as also various physiological changes, have decided influence upon the milk secreted.

	Human milk.		Cow's milk.	
	Variations.	Average.	Variations.	Average.
Water	90.8 to 85.3	88.50	90.2 to 83.7	86.95
Casein and albumin	1.4 to 2.5	2.00	3.3 to 5.5	4.40
Fat (butter)	3.0 to 3.8	3.40	2.8 to 4.5	3.65
Lactose	4.5 to 7.0	5.75	3.0 to 5.5	4.25
Inorganic salts	0.3 to 0.4	0.35	0.7 to 0.8	0.75

	Goat.	Sheep.	Ass.	Mare.	Cream.
Water	86.0	83.3	90.6	90.6	50 to 70
Casein and albumin	3.8	5.4	2.7	2.2	5 to 4
Fat (butter)	5.2	5.3	1.0	1.1	41 to 22
Lactose	4.3	5.2	5.3	5.8	3 to 3
Inorganic salts	0.7	0.8	0.4	0.3	0.7 to 0.7

	Skimmed milk.	Condensed milk.	Butter.	Buttermilk.	Curd.	Whey.
Water	89.6	25	15.0	91.0	59.4	93.8
Casein and albumin	4.2	14	2.2	3.7	27.7	0.8
Fat (butter)	1.0	10	82.0	0.8	6.4	0.3
Lactose	4.4	49[1]	0.3	3.8	5.0	4.5
Inorganic salts	0.8	2	0.5	0.7	1.5	0.6

The inorganic salts consist chiefly of calcium or sodium phosphate and sodium and potassium chloride, but contain also some magnesium and iron. The proteids consist mainly of casein with some albumin, the proportion being about as 6 to 1.

Besides the constituents mentioned in the above analyses, milk also contains a very small quantity of extractives, among which are found peptone, kreatin, leucin, etc. The principles which give to milk its peculiar odor have not yet been conclusively pointed out.

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[1] Including cane-sugar added by the manufacturer.

The gaseous constituents of milk are mainly carbon dioxide, oxygen, and nitrogen. 100 volumes of milk contain of carbon dioxide 7.6, of oxygen 0.1, of nitrogen 0.7 volumes.

Changes in milk. Soon after milk leaves the animal system changes take place which are either of a physical or chemical nature. The first change in milk, when allowed to stand for a few hours, is a separation of the suspended fat globules toward the upper part of the liquid, which gradually becomes loaded with fat, forming a distinct layer over the liquid. This upper layer having a slightly yellowish color (cream color) is *cream*, the watery liquid below having a bluish-white color is *skimmed milk.*

Another change taking place in milk (rarely after a few hours, but generally after a day or a few days) is the coagulation of casein, which takes place both in the cream and in the skimmed milk, converting the whole into a thick, semi-liquid mass, which gradually separates into a solid white *curd*, and a thin, transparent milk-serum or *whey.*

The coagulation of the casein is caused by lactic acid, produced by the so-called lactic fermentation of lactose. The ferments causing this fermentation are undoubtedly floating in the air, as it is possible to prevent the decomposition of milk-sugar for a considerable length of time by taking proper precautions for destroying and excluding them. Simultaneously with the coagulation of milk the alkaline reaction becomes acid and the sweet taste gradually more and more sour.

These changes in milk can, to some extent, be artificially produced, hindered, and controlled. Thus, the casein may be precipitated by the addition of rennet or acetic acid (or any mineral acid) and heating. The decomposition of the milk-sugar and with it the "curdling" may be prevented—1, by chemical treatment with alkaline salts or antiseptics; 2, by physical treatment, such as cooling or icing, boiling and aëration; 3, by condensation or evaporation, with or without the addition of a preservative agent. All these systems of preservation, however, are subject to serious disadvantages because they either interfere with the natural constitution and properties of the milk, or because they serve their purpose for too limited a time.

The addition of alkalies such as lime-water, sodium carbonate or bicarbonate, does not prevent the lactic fermentation, but prevents the action of the liberated acid on the casein by forming a lactate of calcium or sodium.

Of antiseptics, salicylic acid has been used with good results (2 grains to a pint), but it should be remembered that salicylic acid is not absolutely harmless.

Of all preservatives, cold is the most efficient and least objectionable, and milk when cooled to within a few degrees of the freezing-point may be kept for eight to twelve days sweet and without change.

The condensation of milk is effected either simply by evaporating (generally in vacuum pans) a portion of the water, or by first dissolving in it a certain quantity of sugar (generally cane-sugar) and then evaporating to the consistence of a thick syrup, which is placed in suitable air-tight jars. The sugar which is added serves as an additional preventive of decomposition.

The following gives the constituents of milk which may be obtained from it by mechanical processes after it has been changed as described above :

Cream, 20	Butter	3.5 parts.
	Buttermilk	16.5 "
Skimmed milk, 80	Curd	8.0 "
	Whey	72.0 "

Butter. Even in the thickest varieties of cream there is no cohesion between the fat globules, whilst in butter the fat has actually cohered. This change is accomplished by violently agitating (churning) the cream, when the fat particles gradually combine with each other, whilst the liquid (buttermilk) separates.

Chemically, butter is a milk-fat, a mixture of different fats or glycerides of the fatty acids, chiefly palmitic and oleic acids, with small quantities of butyric, caprionic, caprylic, and stearic acids ; it always contains a certain proportion, 15 or 16 per cent., of water, besides traces of casein, salts, coloring matter, etc.

For curing butter, common salt is often used ; the quantity added should not exceed 5 per cent.

The composition of buttermilk has been given above ; when freshly obtained from sweet cream it is a pleasant drink and a wholesome food.

Cheese consists mainly of casein, milk-fat, water, and inorganic salts ; these constituents vary as follows :

Water	61 to 28 parts.
Casein	15 to 35 "
Fat	20 to 30 "
Salts	4 to 7 "

Cheese is made either from pure milk, from skimmed milk, or from a mixture of milk and cream, and accordingly varies considerably in composition. Practically, cheese is made by causing milk to coagulate (either by allowing it to stand or by the addition of rennet, acids, or other substances), and separating the curd (casein and fat) from the whey by mechanical means, such as filtering and pressing. The curd is placed in suitable moulds and afterward allowed to stand or "ripen" for a shorter or longer period. The process of ripening is a partial decomposition (decay and putrefaction) of the casein, and the value of cheese depends mainly upon the nature of the products formed during this decomposition.

Adulterations of milk. Of these, the most commonly practised are removal of cream, addition of water, or both. Sometimes sodium carbonate, sugar, and even chalk are added, but these latter adulterations are fortunately but rarely practised by milk-dealers. The question whether or not milk has been tampered with is generally decided by ascertaining whether cream has been removed or water added. It is, therefore, chiefly the quantity of total solids which has to be determined in order to decide the purity of milk. But it has been shown by the above tables of milk analyses that the quantity of these solids varies considerably, and a minimum of total solids should, therefore, be adopted legally. While no such minimum quantity is officially recognized in many States of this country, it is safe to say that milk containing less than 11 per cent. of total solids may be looked upon as adulterated. (The above given lowest quantity of 9.8 per cent. of total solids in cow's milk is very abnormal.) The methods for detecting such fraud will now be considered.

Testing milk. There is, unfortunately, no instrument which will indicate the purity or quality of milk directly. An instrument used for that purpose, and known as the *lactometer*, is simply a hydrometer which indicates the specific gravity of milk. There are, however, in milk substances which have a tendency to increase the specific gravity, such as lactose, salts, and casein, whilst there is at the same time one substance, the fat, which is specifically lighter than water. The specific gravity of milk ranges from 1.027 to 1.034, the average being about 1.030. If water be added to milk, the specific gravity will become lower, but the same effect may be obtained by adding fat or cream. Again, if cream be removed, the specific gravity will be higher, and in order to bring the milk back to the standard of 1.030, water may be added. In other words, cream may be removed from, and water added to, the same milk and the specific gravity will be unchanged; or a natural milk containing large quantities of fat has the same specific gravity as a poorer milk to which water has been added.

These facts show that the lactometer alone is of no value whatever in milk analysis, although it is useful when the quantity of cream has also been determined. This is generally accomplished by the so-called *creamometer*, a glass tube or glass cylinder about one foot long, half an inch in diameter, and graduated into 100 parts by volume, the 0 being about an inch from the top. The tube is filled with milk to the 0 and set aside for 12 or 18 hours, when the line of demarcation between the cream and the liquid below is well defined and may be easily read off.

The quantity of cream varies from 8 to 20 per cent., but should not fall below 10 per cent. Milk which shows a large quantity of cream (15 to 18 per cent.) may fall considerably below 1.030 in specific gravity, but if there is little cream (8 to 10 per cent.) and the milk shows a low specific gravity, there can be little doubt that it has been tampered with.

There are a number of other instruments, the so-called "*lactoscopes*," used for the determination of cream, the operations of which are based on the fact that milk rich in cream is a much more opaque (or more white) fluid than that from which cream has been taken or to which water has been added.

The above methods of determining the purity of milk, although answering for ordinary purposes, are absolutely insufficient for scientific purposes or as evidence upon which to base legal proceedings. In such cases a complete analysis, including the exact determination of total solids and of various constituents, is required.

Analysis of milk. The total solids are determined by placing a weighed quantity (from 5 to 10 c.c.) of the well-mixed milk in a weighed platinum dish and heating for several hours in a water-bath until no more weight is lost. The loss in weight represents the *water*, the weight of the residue the *total solids*. The *fat* is determined by extracting the solid residue repeatedly with warm ether, filtering this solution through a small filter, which is to be well washed with ether, and evaporating the ethereal solution in a weighed platinum dish.

Milk-sugar is next determined by treating the residue (from which fat has been extracted) with hot diluted alcohol; lactose and a few soluble salts enter into solution; the liquid evaporated to dryness in a weighed dish gives the quantity of sugar plus some salts. Upon igniting the milk-sugar a residue of salts is left, which is also weighed, and this weight deducted from the first one.

Casein. The residue now left (after treatment with ether and alcohol) contains chiefly casein with some albumin and salts. If any casein should have been washed upon the filters accidentally, it has to be transferred back to the dish, the contents of which are dried and weighed. By burning off the casein and reweighing the dish plus the salts, the quantity of the casein is determined.

The remaining salts added to those previously obtained from the alcoholic solution form the *total ash* or *inorganic solids*, an analysis of which may be made according to the methods given heretofore.

Casein may also be determined directly by precipitating it from milk, by the addition of acetic acid and boiling. The precipitated casein is filtered off, and has to be well washed, first with water, and then with ether, as it contains most of the fat.

Experiment 68. *a.* Determine the specific gravity of milk, cream and skimmed milk by means of the lactometer (a urinometer answers the purpose).

b. Acidulate some skimmed milk with acetic acid, notice the coagulation of the casein, and separate it from the whey by filtering through paper or cloth, using some pressure to expel most of the liquid.

c. Test the casein by heating with nitric acid (yellow color), by using Millon's reagent (purple-red color), by warming gently on the water-bath with concentrated hydrochloric acid (violet-colored solution), by warming gently with water and a few drops of potassium hydroxide, when a solution is obtained from which the casein is reprecipitated on neutralizing with acetic acid.

d. Test the whey for milk-sugar by heating with Fehling's solution (red precipitate), by applying Moore's test, *i. e.*, heating with potassium hydroxide (brown color), and by heating with solution of picric acid and potassium hydroxide (reddish-brown color).

e. Determine the constituents of milk quantitatively by using the directions given above.

QUESTIONS.—531. Mention the five principal constituents of milk. 532. Give the average composition of human and of cow's milk. 533. What compounds constitute milk-ashes? 534. What physical and what chemical changes does milk suffer on standing? 535. What acid is formed in milk on standing, and how does this acid act on the casein? 536. Describe the processes used for preventing the decomposition of milk. What are their advantages and their disadvantages? 537. Give approximately the quantities of the chief components of cream, skimmed milk, butter, buttermilk, curd, whey, and cheese, and state how these substances are obtained. 538. Why does the specific gravity of milk not indicate its purity and richness? 539. Describe the advantages of the combined use of the lactometer and creamometer in testing milk. 540. Give a process for the complete quantitative analysis of milk.

55. URINE AND ITS NORMAL CONSTITUENTS.

Secretion of urine. It has been explained in a former chapter how blood absorbs the digested food as chyle, how this is acted upon by the atmospheric oxygen in the lungs, and how this arterial blood, whilst passing through the system, deposits proteids and other substances, receiving in exchange the products formed by the oxidation of the various tissues. These products are either gases (chiefly carbon dioxide), liquids (chiefly water), or solids held in solution by the water. These waste solids must necessarily be eliminated from the system, and the organs which accomplish this result are the kidneys.

The process of separating the waste materials from the blood is chiefly of a physical nature, partly a transudation or filtration, and partly a diffusion or osmose. The conditions essential for such an exchange are given in the kidneys. Blood is separated by delicate membranes from a thin, aqueous, saline solution; the interchange taking place is chiefly a passage of the waste crystalline products of the blood into the aqueous solution, which is thereby gradually converted into urine, that liquid, which is finally discharged, carrying off nearly the total quantity of all the nitrogen taken into the system in the form of nitrogenous food.

General properties. Normal human urine, when in a fresh state, is a clear, transparent aqueous liquid, of a lighter or deeper amber color, having a peculiar, faintly aromatic odor, a bitter, saline taste, a distinct acid reaction on blue litmus-paper, and a specific gravity heavier than water (average about 1.020). When urine is kept in a clean vessel it may remain unchanged for several days, provided the temperature be not too high, and the amount of total solid constituents not too small.

In urine, shortly after cooling, especially if it be concentrated, a light, cloudy film of mucus is formed, which slowly sinks to the bottom; the acid reaction gradually increases, small yellowish-red crystals of acid urates, or uric acid, are deposited. In this condition the urine may often continue unchanged for several weeks, provided the temperature be low. If, however, the urine be very dilute, and the temperature above the mean, decomposition speedily takes place. The urine is then found to be covered with a thin, shining, and frequently iridescent membrane, fragments of which sink gradually to the bottom. The urine then becomes turbid, acquires a pale color, its reaction becomes alkaline, and it begins to develop a nauseous ammoniacal odor, due to the products formed by the decomposing action of certain microörganisms (chiefly bacterium ureæ and micrococcus ureæ) upon urea, which is converted into ammonium carbonate. The change from an acid to an alkaline urine causes the precipitation of earthy phosphates, ammonium-magnesium phosphate, ammonium urate, etc.

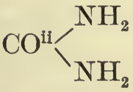
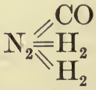
Composition. Urine is chiefly an aqueous solution of urea and inorganic salts, containing, however, always some uric acid, mucus, coloring and other organic matters. The average composition of normal human urine may be stated thus:

Water	95.76 per cent.
Urea	2.50 "
Uric acid	0.04 "
Hippuric acid Kreatin Kreatinin Coloring matter Mucus Unknown organic matters	0.40 per cent.
Phosphates Chlorides Sulphates of sodium potassium calcium magnesium iron	1.30 per cent.

The above average composition of human urine varies considerably, and is influenced by the water and food taken, amount of work done, time of day, temperature of air, age, sex, etc.

Urine also contains gaseous constituents, amounting to about 16 per cent. by volume; these gases are chiefly carbon dioxide (88 per cent.), and nitrogen (11 per cent.), with very little oxygen (1 per cent.).

The quantity of urine passed in a day also varies widely, an adult discharging from 500 to 2300 c.c. in twenty-four hours; a normal average quantity is about 1400 to 1600 c.c. (about 49 to 56 ounces). The quantity of total solids contained in this urine varies from 55 to 60 grammes (840 to 920 grains), and over one-half of this quantity is urea.

Urea, Carbamide, COH_4N_2, or  $CO^{II}<\begin{matrix}NH_2\\NH_2\end{matrix}$ or  $N_2\begin{matrix}=CO\\=H_2\\=H_2\end{matrix}$ or $CO(NH_2)_2$. Urea is the most important constituent of urine, and is the substance which carries off by far the largest quantity of all nitrogen taken in the food. Urea has never yet been found as a product of vegetable life, but is found as a normal constituent of the urine of the mammalia, and in smaller quantity in the excrement of birds, fishes, and some reptiles. It occurs also in blood, muscular tissue, chyle, lymph, bile, perspiration, and many other animal fluids.

When pure, urea crystallizes from an aqueous solution in colorless prisms; it is odorless, and has a cooling, bitter taste; it easily dissolves in water, the solution having a neutral reaction; it fuses when heated to 130° C. (266° F.), but decomposes at a higher temperature, giving off ammonia gas and water, whilst a number of other substances are formed at the same time. A pure solution of urea does not decompose at ordinary temperature, but on boiling, and especially under pressure, it takes up water, and is decomposed into ammonia and carbon dioxide, or into ammonium carbonate:

$$CO(NH_2)_2 + 2H_2O = CO_2 + 2NH_3 + H_2O = (NH_4)_2CO_3.$$

The same decomposition takes place in urine under the influence of a ferment (most likely present in urine, or perhaps derived from the air), if the temperature be not too low.

A solution of urea is decomposed by the action of chlorine or bromine with generation of hydrochloric (or hydrobromic) acid, carbon dioxide, and nitrogen:

$$CO(NH_2)_2 + 6Cl + H_2O = 6HCl + CO_2 + 2N.$$

Alkali hypochlorites or hypobromites cause a similar decomposition, upon which is based the quantitative estimation of urea.

Urea forms with acids definite salts, and with certain oxides and salts definite compounds.

Urea is formed artificially by numerous decompositions, as, for instance:

a. By a process similar to the one taking place in the animal system, viz., by limited oxidation of albuminous substances by potassium permanganate.

b. By oxidation of uric acid in the presence of water:

$$\underset{\text{Uric acid.}}{C_5H_4N_4O_3} + H_2O + O = \underset{\text{Urea.}}{CO(NH_2)_2} + \underset{\text{Alloxan.}}{C_4H_2N_2O_4}.$$

c. By the action of caustic alkalies upon kreatin:

$$\underset{\text{Kreatin.}}{C_4H_9N_3O_2} + H_2O = \underset{\text{Urea.}}{CO(NH_2)_2} + \underset{\text{Sarcosine.}}{C_3H_7NO_2}.$$

d. By the molecular transformation of ammonium cyanate, which takes place when its solution is evaporated and allowed to crystallize:

$$NH_4.CNO = CO(NH_2)_2.$$

e. By the action of carbonyl chloride, $COCl_2$, on ammonia:

$$COCl_2 + 2NH_3 = 2HCl + CO(NH_2)_2.$$

f. By the action of ammonia on ethyl carbonate:

$$(C_2H_5)_2CO_3 + 2NH_3 = 2(C_2H_5OH) + CO(NH_2)_2.$$

Urea may be obtained from urine by evaporating it to the consistence of a syrup and mixing the cooled residue with an equal volume of nitric acid, when crystals of urea nitrate, $CO(NH_2)_2.HNO_3$, form, which may be decomposed by barium carbonate into urea and barium nitrate:

$$2[CO(NH_2)_2.HNO_3] + BaCO_3 = CO(NH_2)_2 + Ba(NO_3)_2 + CO_2 + H_2O.$$

Experiment 69. Evaporate about 200 c.c. of urine to a syrupy consistence, allow to cool, place the vessel containing the syrup in ice and add slowly with stirring a volume of nitric acid equal to that of the evaporated urine. Set aside for twenty-four hours, collect the crystalline mass of urea nitrate on a filter, wash with very little cold water, allow to drain well and dissolve in hot water. (If much colored, shake the solution with animal charcoal and filter.) To the hot solution add freshly precipitated barium carbonate as long as carbon dioxide escapes. Filter and evaporate the solution to dryness over a water-bath; boil the mass with alcohol, which dissolves the urea, but does not act on the barium nitrate. Allow the urea to crystallize from the alcoholic solution.

Reactions and determination of urea. There are no very characteristic reactions by which urea can be well recognized. From organic mixtures it is separated by digesting them with from 3 to 4 volumes of alcohol in the cold; the filtered liquid is evaporated to dryness and extracted with alcohol, which again is evaporated. The dry residue may be tested for urea as follows:

1. Dissolved in a few drops of water, the addition of an equal quantity of colorless nitric acid causes the formation of white, shining, crystalline plates or prisms of urea nitrate.

2. If a strong solution of oxalic acid is added, instead of nitric acid, rhombic plates of urea oxalate form.

3. The residue (or urea) heated in a test-tube to about 160° C. (320° F.) until no more vapors of ammonia are evolved, leaves a substance termed *biuret*, $C_2H_6N_3O_2$, which upon the addition of a few drops of potassium hydroxide solution and a drop of cupric sulphate solution, causes the solution of the cupric hydroxide with a reddish-violet color.

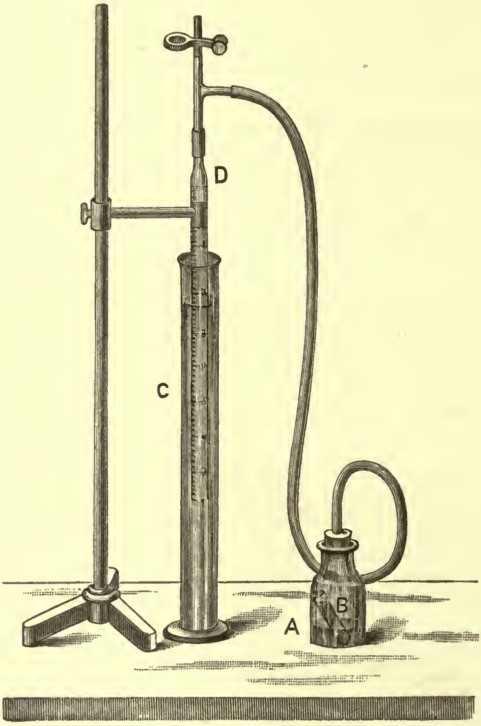
The *quantitative estimation of urea* in urine may be effected by various methods, of which but one will be mentioned, because it requires less time and less skill in manipulation than most other methods. This determination is based upon the fact that urea is decomposed by alkali hypobromites into carbon dioxide, water, and nitrogen:

$$CO(NH_2)_2 + 3(NaBrO) = 3NaBr + CO_2 + 2H_2O + 2N.$$

The liberated nitrogen is collected, and from its volume its weight and that of the urea are calculated.

Practically, the operation is conducted as follows: 100 grammes of sodium hydroxide are dissolved in 250 c.c. of water, and to this cooled solution are added 25 c.c. of pure bromine, when sodium hypobromite is formed, leaving, however, an excess (over one-half) of the sodium hydroxide in an unaltered condition. (The solution easily decomposes, and should, therefore, be freshly prepared for analysis.)

FIG. 41.



Apparatus for the volumetric estimation of urea.

The apparatus required (Fig. 41) consists, in its most simple form, of a wide-mouth bottle, A; a small test-tube, B, of about 10 c.c. capacity; a glass cylinder, C, and a graduated burette, D.

Into a bottle is fitted a perforated cork, which is connected by means of tubing with the burette. 5 c.c. of urine are introduced into the test-tube and 20 c.c. of the alkali hypobromite solution into the bottle, care being taken not to bring the liquids in contact with each other. The graduated burette is lowered in the cylinder, until the zero-mark is on a level with the surface of the water in the cylinder and the connection between the burette and the bottle made. By now inclining the bottle so that the urine comes in contact with the hypobromite, decomposition of urea takes place energetically. The liberated carbon dioxide is absorbed by the sodium hydroxide, while the nitrogen increases the volume of air present in the apparatus. The burette is gradually raised as the nitrogen is evolved, and the whole allowed to stand for half an hour. The cubic centimeters of nitrogen gas are read off (whilst the water in the burette and cylinder are on a level), and give, multiplied by 0.0027, the grammes of urea in 5 c.c. of urine.

As the volume of gas depends upon temperature and pressure, corrections for these have to be made by using the following formula:

$$p = \frac{100\,v\,b}{760.370.\,a\,(1 + 0.003665t).}$$

p = Weight of urea for 100 c.c. urine.
a = Volume of urine used, expressed in c.c.
v = Volume of nitrogen read off.
b = Barometric pressure in mm.
t = Temperature during the measurement of nitrogen.
370 represents the c.c of nitrogen (at 0° and 760 mm pressure) obtained from one gramme of urea.

The above described process for estimation of urea is, for various reasons, far from being perfect (uric acid and kreatin, for instance, are also decomposed with liberation of nitrogen; but it has been found that the results obtained are quite sufficient for clinical purposes.

Experiment 70. Determine urea in urine by the method described above.

Uric acid, $H_2C_5H_2N_4O_3$. Uric acid is found in small quantities in human urine, chiefly in combination with sodium, potassium, and ammonium, but also with calcium and magnesium. In larger proportions, uric acid is found in the excrement of birds, mollusks, insects, and chiefly of serpents, the solid urine of the latter consisting almost entirely of uric acids and urates. It is also found in Peruvian guano.

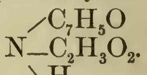
Pure uric acid is a white, crystalline, tasteless, and odorless substance, almost insoluble in water, requiring 1900 parts of boiling and 15,000 parts of cold water for its solution; it is also insoluble, or nearly so, in alcohol and ether. The great insolubility of uric acid causes its separation in the solid state, both in the bladder and in the tissues.

Reactions and determination of uric acid. Uric acid may be recognized by its crystalline form, and by the *murexid test,* which is made by placing a fragment of uric acid in a porcelain dish, adding a drop of nitric acid, and carefully evaporating over a flame. To the dry residue a drop of ammonia water is added, which produces a beautiful purplish-red color. (Plate VIII., 4.) This reaction occurs, however, also with a number of substances which are similar to, but more complex in composition than uric acid.

The *quantitative estimation of uric acid* in urine is best accomplished by adding 10 c.c. of hydrochloric acid to 250 c.c. of urine, setting aside for 24 hours in a cool place, and collecting the crystals of uric acid on a small filter which has been previously weighed. The crystals are washed with a little water, and dried at 100° C. (212° F.). As uric acid is not entirely insoluble, 0.0038 gramme has to be added for every 100 c.c. of urine employed for the analysis.

If the urine (to be tested for uric acid) be very dilute, it should be evaporated to about one-half its bulk before adding hydrochloric acid; if it contain albumin, this should be removed by adding a drop of acetic acid, boiling and filtering.

Hippuric acid, $C_9H_9NO_3$ (*Benzyl-glycocol, Benzyl-amido-acetic acid*), is a normal constituent of human urine, but is found in much larger quantities in the urine of herbivora. Its constitution may be considered as ammonia in which two hydrogen atoms are replaced by the radicals of benzoic and acetic acid respectively, thus,



$$\mathrm{N}\begin{array}{l}\diagup C_7H_5O\\ -C_2H_3O_2.\\ \diagdown H\end{array}$$

Hay, and especially aromatic herbs, contain benzoic acid, or compounds having a similar composition, and a portion of these compounds is eliminated in hippuric acid. Administration of benzoic acid increases the amount of hippuric acid in urine.

When pure, hippuric acid crystallizes in transparent, colorless, odorless prisms, which have a bitter taste, and are sparingly soluble in water.

Analytically, hippuric acid is characterized—

1. By giving a sublimate of benzoic acid, and an odor of hydrocyanic acid, when heated in a dry test-tube.
2. By giving a brown precipitate with ferric chloride.
3. By giving off benzene and ammonia when heated with calcium hydroxide.
4. By evolving an intense odor of nitro-benzene when evaporated to dryness with a few drops of nitric acid.

Other organic substances, such as kreatin, kreatinin, xanthin, lactic acid, mucus, coloring matters, etc., occur in such small quantities in normal urine that their detection, separation, and quantitative estimation are very difficult, and are almost exclusively attempted during scientific investigations.

56. EXAMINATION OF NORMAL AND ABNORMAL URINE.

Points to be considered in the analysis of urine. They are:

1. Color, odor, general appearance—whether clear, smoky, cloudy, turbid, etc.
2. Reaction—whether acid, neutral, or alkaline to test-paper.
3. Specific gravity.
4. Total amount of organic and inorganic solids.
5. Total amount of inorganic matter (ash).
6. Determination of urea.
7. Determination of uric acid.
8. Determination of inorganic acids and bases. (Hydrochloric, sulphuric, and phosphoric acids; sodium, potassium, calcium, magnesium, and iron.)
9. Determination of albumin.
10. Determination of sugar.
11. Examination for bile.
12. Examination of any organic or inorganic sediment, either by chemical means or by the microscope.

Samples of urine should always be drawn from the well-mixed and exactly measured quantity of the total urine discharged in twenty-four hours.

Color. Normal urine is generally pale-yellow or reddish-yellow, but it may be as colorless as water, or as dark brownish-black as

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QUESTIONS.—541. What is urine, where and by what process is it formed in the animal body, and what is its function? 542. Mention the general physical and chemical properties of urine. 543. Give the average composition of human urine, and state by what conditions the composition is influenced. 544. State the composition and properties of urea. 545. By what process is urea formed in the animal body, and how can it be obtained artificially? 546. Describe a process by which urea may be estimated quantitatively in urine. 547. In what forms is uric acid found in urine, and what are its properties? 548. Describe the murexid test. 549. How can uric acid be determined quantitatively in urine? 550. What is hippuric acid, and by what tests may it be recognized?

porter; a reddish and smoky tint generally indicates the presence of blood, and a brownish-green suggests the presence of the coloring matter of bile. (Plate VIII., 1–3.)

The true nature of the normal coloring matters of urine is as yet doubtful; the existence of at least two has, however, been demonstrated; they have been named *urobilin* and *urochrome*, and are, most likely, products of the decomposition of biliary matters.

Abnormal coloring matters are chiefly those of blood, bile, and of certain vegetables; thus, rhubarb and senna leaves cause a reddish-yellow to deep red color, especially in alkaline urine; santonin produces a bright-yellow color, changing to red or crimson on the addition of an alkali. Carbolic acid introduced into the system causes a dark, or even black discoloration of urine, while large doses of salicylic acid color it green.

The coloring matters of blood may be recognized by adding to a few drops of urine a drop of freshly prepared tincture of guaiacum, and agitating with a solution of ozonized ether (ethereal solution of hydrogen dioxide); the latter is colored blue in case hæmoglobin is present. In place of ozonized ether, oil of turpentine which has been in contact with atmospheric air for some weeks may be used, and the test made by allowing urine to flow down the test-tube containing a mixture of the oil and tincture; a blue coloration will slowly appear, if blood be present. The test has the serious disadvantage that protoplasm in almost any form will give the blue color.

Detection of biliary coloring matter will be considered later.

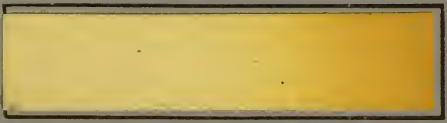
Indican, $C_8H_6N.HSO_4$. This substance is pale-yellow, but yields readily blue indigo by oxidation. It occurs in very small quantities in normal urine, but is much increased in cases of marked intestinal fermentation, also in abdominal diseases, in peritonitis, and especially in obstructions of the bowel.

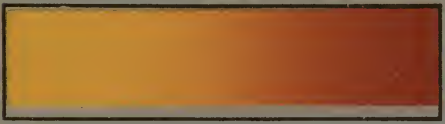
Indican is recognized as follows: Equal volumes of strong hydrochloric (or nitric) acid and urine are mixed in a test-tube, and, drop by drop, while shaking the tube, a freshly-prepared 1 per cent. solution of bleaching powder is added. Normal urine shows a green color only, while large quantities of indican are indicated by a more or less distinct blue color. By shaking the contents of the test-tube with a little chloroform, indican is dissolved by the latter, imparting to it a blue color.

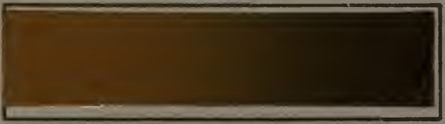
Indigo-red appears in the urine in the same conditions in which indican is found. It is recognized by Rosenbach's reaction: Urine is boiled, and while it is still boiling nitric acid is added drop by

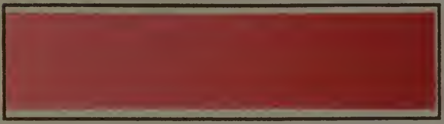
PLATE VIII.

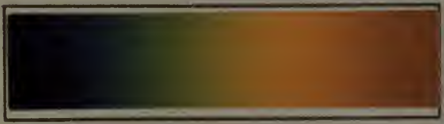
URINE

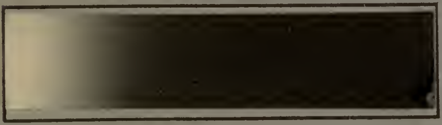
1

Urine tints—Pale yellow, light yellow, yellow.

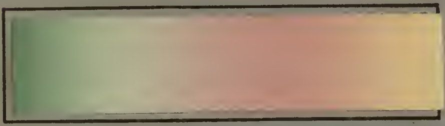
2

Urine tints—Reddish yellow, yellowish red, red.

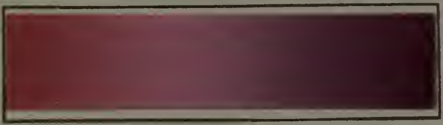
3

Urine tints—Brownish red, reddish brown, brownish black.

4

Murexid test for uric acid.

5

Trommer's or Fehling's test for sugar.

6

Bötger's bismuth test for sugar.

7

Gmelin's test for biliary coloring matters.

8

Pettenkofer's test for biliary acids.

drop, when a deep-red color appears, if indigo-red is present. The foam on shaking the test-tube is bluish-red.

Odor. The normal odor of fresh urine is characteristic, and is sometimes spoken of as aromatic; it is not known by what substance or substances this odor is caused. The ammoniacal and putrescent odor which urine acquires on standing is due to the products of decomposition formed, chiefly ammonia.

A number of substances taken internally and separated by the kidneys from the blood, cause the urine to assume a characteristic odor; aromatic substances especially impart such odors; oil of turpentine gives an odor reminding of violets, and the odor of cubebs, copaiba, asparagus, garlic, valerian, and other substances is promptly transferred to the urine of persons using these drugs internally. A sweetish smell sometimes attends the presence of large quantities of sugar in urine.

Reaction. This is generally acid in healthy urine which has been recently passed, but may become neutral or alkaline within a short period, by decomposition of urea and formation of ammonium carbonate. The acid reaction of urine is due chiefly to monosodium ortho-phosphate, NaH_2PO_4, and perhaps also to the acid salts of uric acid.

The acidity may be determined volumetrically by the addition of deci-normal solution of sodium or potassium hydroxide to 100 c.c. of urine, using litmus-paper as an indicator. The acidity of urine is generally expressed as oxalic acid, of which 1 c.c. of normal potash solution neutralizes 0.0063 gramme. If, for instance, 100 c.c. of urine require 15 c.c. of deci-normal potash solution, then the acidity of the 100 c.c. urine is $15 \times 0.0063 = 0.0945$; and for the total urine of the 24 hours—say 1800 c.c.—the acidity expressed as oxalic acid is, therefore, equal to 1.701 grammes.

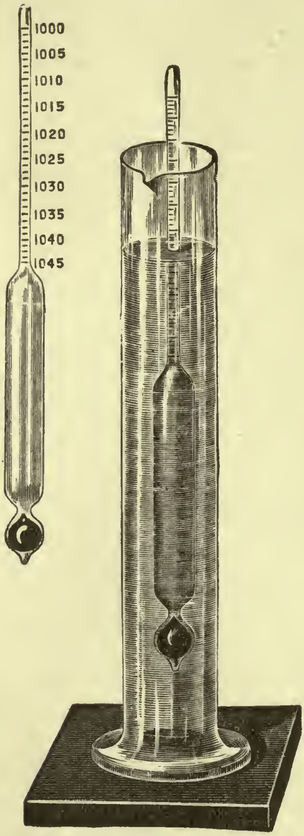
While urine shows an acid reaction generally, it may have a neutral or even alkaline reaction. In many cases this alkaline reaction points to decomposition of urea in the bladder, but it may be due also to the elimination of alkali carbonates, derived from food taken or drugs administered.

Thus, the alkali tartrates, citrates, acetates, etc., have (after digestion) a tendency to neutralize uric acid, and an excess of them is eliminated as carbonate.

To distinguish between the harmless alkaline reaction caused by fixed alkalies and the alkaline reaction produced by decomposition of urea, a piece of red litmus-paper may be used. If this, after having been moistened with the urine, remains blue on drying (by warming gently) the reaction is due to the fixed alkalies; if the red color reappears, the alkaline effect is due to ammonia compounds.

Urine sometimes is amphoteric in its reaction, *i. e.*, it colors red litmus-paper faintly blue, and blue litmus-paper slightly red. This condition is caused most likely by the simultaneous presence of monosodium orthophosphate, NaH_2PO_4, which has an acid, and of disodium orthophosphate, Na_2HPO_4, which has an alkaline reaction.

FIG. 42.



Urinometer.

Experiment 71. Prepare normal soda solution as directed on page 258, dilute it with 9 parts of water, and titrate with this deci-normal solution 100 c.c. of urine, using litmus-paper as an indicator.

Specific gravity. The normal specific gravity of an average amount of 1500 c.c. of urine passed in twenty-four hours is about 1.020, but it varies, even in health, from 1.012 to 1.030 or more. A specific gravity above 1.030 may indicate the presence of sugar, larger quantities of which may cause the specific gravity to rise to 1.050. Albuminous urine is frequently of low specific gravity, 1.010 to 1.012.

It should be remembered that the specific gravity of urine considered separately from the quantity of urine passed in twenty-four hours is of no value, and that in some diseases (for instance in acute nephritis with albuminuria) the specific gravity of albuminous urine may be as high as 1.030, while a diabetic urine may have a specific gravity of 1.025, or less, in consequence of a large volume passed.

The determination of the specific gravity of urine is generally accomplished by the *urinometer*, which is a small hydrometer indicating specific gravity from zero (or 1000) to 60 (or 1060). (See Fig. 42.) As the temperature influences the density of liquids, a urinometer can only give correct results at a certain degree of temperature, which is generally marked upon the instrument.

Determination of total solids. An approximate determination of total solids may be deduced from the specific gravity of the urine, as it has been found that the last two figures of the specific gravity of urine, multiplied by 2.33, correspond to the number of grammes in 1000 c.c. of urine. If, for instance, 1450 c.c. of urine, of a specific gravity of 1.018, have been discharged in twenty-four hours, then the quantity of total solids in 1000 c.c. will be 18 × 2.33, or 41.94 grammes; and in 1450 c.c. 60.81 grammes.

A more exact method of determining the total solids in urine is the evaporation of about 10 c.c. in a weighed platinum dish over a water-bath (or, better, under the receiver of an air-pump over sulphuric acid), until it is found that no more loss in weight ensues on continued exposure of the dish in the drying apparatus. By now reweighing the dish, plus contents, and deducting from the weight that of the empty dish, the weight of total solids is found.

Determination of inorganic constituents. The platinum dish containing the known quantity of total solids is exposed to the action of a non-luminous flame, and the heat continued until all organic matter has been destroyed and expelled. By reweighing now, and deducting the weight of the platinum dish, plus ash, from the weight of the dish, plus total solids, the quantity of total organic matter is determined; and by deducting weight of dish from weight of dish plus ash, the total quantity of inorganic matter is found.

Experiment 72. Determine total solids, water, total organic and inorganic matters in a specimen of urine by following the directions given above. Use 10 or 20 c.c. of urine for the analysis.

The analysis of the ash is effected by the methods given in connection with the consideration of the various acid and basic constituents themselves. *Chlorine* is determined by precipitating the solution of the ash in nitric acid with silver nitrate, *sulphuric acid* by barium chloride, *phosphoric acid* by ammonium molybdate, *calcium* by ammonium oxalate, *potassium* by platinic chloride, *iron* by potassium ferrocyanide, etc.

For the determination of many of the inorganic constituents, it is not necessary to destroy the organic matter as described above, but this determination can be effected directly. Thus, *chlorine* may be precipitated directly from urine (slightly acidulated with nitric acid) by silver nitrate; the precipitated silver chloride is collected upon a small filter, well washed, dried, and weighed in a porcelain crucible, after the filter (to which particles of silver chloride adhere) has been burned separately and its ash added to the contents of the crucible, which is moderately heated before weighing.

Experiment 73. Determine the amount of sodium chloride solution volumetrically by means of potassium sulphocyanate as follows: Place 5.837 grammes (about 5.7 c.c.) of urine into a 150 c.c. flask, add 2 c.c. of nitric acid, 20 c.c. of water, and 15 c.c. of deci-normal silver nitrate solution. Mix well, add some ferric alum solution, and then from a burette deci-normal potassium sulphocyanate solution until, after frequent shaking of the flask, the white precipitate coheres in curdy masses, and the liquid assumes a red tint. The number of c.c. of sulphocyanate required is then deducted from the 15 c.c. of silver nitrate added at first, and the difference shows the number of c.c. of silver nitrate required to precipitate the sodium chloride in the urine. Normal urine requires from 8 to 11 c.c. silver solution, each c.c. corresponding to 0.1 per cent. of sodium chloride. (For explanation of the method see page 269.)

Phosphoric acid is found in urine, in part (about two-thirds) combined with alkalies, and in part (about one-third) with lime and magnesia. These phosphates have in acid or neutral urine the composition NaH_2PO_4, Na_2HPO_4, $CaHPO_4$, $CaH_4(PO_4)_2$, $MgHPO_4$; in alkaline urine compounds of the composition Na_3PO_4, $Ca_3(PO_4)_2$, $Mg_3(PO_4)_2$, $MgNH_4PO_4$ may be present.

By adding any alkali the phosphates of calcium and magnesium (generally termed earthy phosphates) are precipitated, the phosphates of sodium or possibly potassium remain dissolved.

The so-called *earthy phosphates* (phosphates of calcium and magnesium) may be approximately determined by adding a few drops of an alkaline hydroxide to about 50 c.c. of urine, heating to the boiling-point, collecting on a filter, washing, igniting, and weighing in a platinum crucible.

Experiment 74. Add to 50 c.c. of urine a few drops of calcium chloride solution and then water of ammonia. Phosphoric acid is completely precipitated, chiefly as tricalcium phosphate, $Ca_8(PO_4)_2$, containing, however, a very small quantity of magnesium ammonium phosphate. Collect the precipitate on a filter, wash well, dry, ignite and weigh it. Calculate the phosphoric acid from the tricalcium phosphate, without reference to the small amount of magnesium phosphate.

Experiment 75. Add to 100 c.c. clear urine 5 c.c. hydrochloric acid; boil, and then add barium chloride to complete precipitation. Set aside for one hour, filter, wash well, dry, ignite and weigh. Calculate from the weight of barium sulphate, thus obtained, the percentage of sulphuric acid present in the urine examined.

The methods for estimating *urea* and *uric acid* have been described in the preceding chapter.

Detection of albumin. Serum-albumin and serum-globulin are the forms most frequently present in urine, but peptones and other albuminoids are also met with. The different methods by which the presence of albumin in urine is demonstrated are based upon the coagulation of albumin. This coagulation may be accomplished by heat, by nitric acid, by picric acid, by potassium ferrocyanide in the presence of acetic acid, and also by either metaphosphoric or trichloracetic acid.

The urine used for any of these tests must be perfectly clear; if it be not clear, it must be rendered so by processes which vary according to the nature of the substance causing the turbidity. In most cases filtration through good filter-paper may be sufficient; but if this does not accomplish the desired result, it may become necessary to use other means. Thus, if earthy, amorphous phosphates be present (which, especially in alkaline urine, are apt to pass through the best filter-paper), they may be removed by adding to the urine about a fourth part of potassium hydroxide solution, warming the mixture, and filtering. If the turbidity be caused by urates, the urine will generally become clear by passing the test-tube once or twice through a flame.

The clear urine is then tested by either (or all) of the following methods:

a. Coagulation by heat. A test-tube is filled about one-half with the urine, to which, if not distinctly acid to test-paper, a few drops of acetic acid are added.[1] (In case potassium hydroxide has been added in order to precipitate the phosphates, enough of acetic acid must be added to cause a distinct acid reaction.) The test-tube is then held over the flame in such a manner that the heat acts upon the upper half of the urine only, heating this portion gradually to near the boiling-point. By thus operating, two strata of fluid are obtained for comparison, and by holding the test-tube against the light, or against a black background, any difference in the appearance of the upper and lower strata may be noticed. Any cloudiness or opacity seen may be due to albumin, but may also be caused by earthy phosphates, because these are often precipitated by heating, and have been mistaken for albumin quite frequently.

The reason why phosphates are often precipitated by heating of urine is this: Urine, showing a slightly acid or neutral reaction, contains dicalcium and dimagnesium phosphates, which salts upon heating are decomposed into soluble monophosphates and insoluble triphosphates, thus:

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[1] If acetic acid alone causes a precipitate, this may be due to mucin, which should be filtered off before heating.

$$\underset{\text{Dicalcium phosphate.}}{4CaHPO_4} = \underset{\text{Monocalcium phosphate.}}{Ca(H_2PO_4)_2} + \underset{\text{Tricalcium phosphate.}}{Ca_3(PO_4)_2}$$

To decide the nature of the precipitate a few drops (10 to 15) of nitric acid are allowed to flow gently down the side of the tube into the urine. The precipitate will readily disappear when caused by phosphates, but will be permanent when albumin is present.

Instead of heating, as above described, merely the upper half of the urine, the total quantity of the urine (acidulated by a few drops of acetic acid) may be heated, and the test-tube set aside for several hours (after having added 10 to 15 drops of nitric acid), in order to allow the albumin to subside, when it can be more distinctly seen and its quantity noticed.

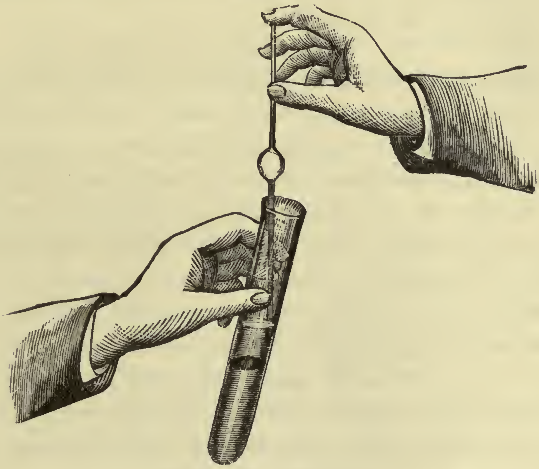
b. Nitric acid test. A test-tube is filled to the depth of about half an inch with colorless nitric acid, and an equal quantity of urine is allowed to flow down the side of the test-tube in such a manner that the specifically lighter urine forms a distinct and separate layer over the nitric acid. (If the urine be allowed to flow from a pipette, as shown in Fig. 43, the formation of the two strata is easily accomplished.) In case albumin is present, a white band or zone of varying thickness (according to the quantity of albumin present) appears at the point of contact.

If the urine be highly concentrated, a similar white zone is formed between the acid and urine, due to the separation of insoluble acid urates; the difference between the separated urates and albumin is that the latter forms a sharply defined zone, whilst the urates diffuse into the urine above. Moreover, the urates dissolve on the application of heat. Finally, the separation of acid urates may be avoided by diluting the urine with an equal volume of water and placing this diluted urine upon the nitric acid.

c. Picric acid test for albumin. This test has the advantage that neither phosphates nor urates can be mistaken for albumin. It consists in slowly dropping urine into a test-tube filled to about one-fourth with a highly colored solution of picric acid in water. In the presence of albumin a white cloud or sharply defined white turbidity is formed, and on warming the liquid the albumin collects into balls which rise to the surface of the liquid.

d. Potassium ferrocyanide test. 5 to 10 c.c. of cold urine are acidulated with 5 to 10 drops of acetic acid, and to the mixture are added a few drops of solution of potassium ferrocyanide. In the presence of even traces of albumin a turbidity is caused. This test is extremely delicate, especially when modified so as to allow a few c.c. of diluted acetic acid, to which a few drops of potassium ferrocyanide solution had been added, to flow down the side of the test-tube containing the urine. A decided turbidity at the point of contact of the two liquids shows albumin.

FIG. 43.



Nitric acid test for urine.

In case the addition of acetic acid to the cold urine should cause a turbidity (which may be due to mucin) it must be filtered before adding the potassium ferrocyanide.

e. Metaphosphoric acid (glacial phosphoric acid) or *trichlor-acetic acid* may be used for the detection of albumin by dropping a fragment of either substance into a few c.c. of urine contained in a test-tube. As the acids dissolve, a cloudy ring forms in the presence of albumin, which is not dissolved on warming.

f. Tanret's test is made by means of a solution containing of potassium iodide 3 32 grammes, mercuric chloride 1.35 grammes, acetic acid 20 c.c. in a sufficient amount of water to make 100 c.c. For *Millard's test* is required a solution made by mixing 2 parts of carbolic acid with 7 parts of glacial acetic acid and 22 parts of potassium hydroxide solution. Both solutions give on heating precipitates with albumin, even when present in very small quantity.

In the above methods the manipulations and precautions are minutely described, in order to detect small quantities or even traces of albumin. When albumin is abundantly present, there is no difficulty whatever in its detection, as heat will precipitate it from an acid, neutral, or sometimes even alkaline urine; the precipitate should, however, always be tested by the addition of a few drops of nitric acid, and the previous addition of a few drops of acetic acid is also advisable.

A neutral urine should never be acidified by nitric acid (instead of acetic acid), because a drop or two of nitric acid may in some cases prevent the coagulation of albumin by heat, though a larger quantity (10 to 20 drops) has no such effect.

Quantitative estimation of albumin. The average amount of albumin present in acute cases of albuminuria is 0.1 to 0.5 per cent., rarely over 1 per cent., though it may rise to 4 per cent. An approximate method for the comparative estimation of albumin is to precipitate it (with the precautions above given) in a graduated test-tube by heat and setting aside for twelve (or better for twenty-four) hours. At the end of that time the proportion of the coagulated albumin which has collected at the bottom of the fluid is noticed. If the albumin occupy one-fourth, one-sixth, one-tenth of the height of the liquid, there is said to be one-fourth, one-sixth, or one-tenth of albumin in the urine. If, however, at the end of twelve or twenty-four hours scarcely any albumin has collected at the bottom, there is said to be a trace.

The volumes of coagulated albumin indicate the following quantities of dry albumin:

Slight turbidity indicates about	0.01	per cent.
$\frac{1}{20}$ of the tube is filled	0.05	"
$\frac{1}{10}$ " "	0.10	"
$\frac{1}{4}$ " "	0.25	"
$\frac{1}{3}$ " "	0.50	"
$\frac{1}{2}$ " "	1.00	"
Complete coagulation	2 to 3	"

A better method of exactly estimating the amount of albumin is its complete separation and weighing, as described below.

Experiment 76. Acidify 100 c.c. of clear albuminous urine with acetic acid; heat to the boiling-point in a water-bath for half an hour, and filter through a small filter, previously dried at 110° C. (230° F.) and weighed; wash with boiling water to which a little ammonia water has been added (to remove uric acid and urates), then with pure water until the filtrate is not rendered turbid any longer by silver nitrate, next with pure alcohol, and finally with ether. Dry and filter contents at 110° C. (230° F.) and weigh.

As it may happen that the precipitated albumin encloses earthy phosphates, it is well to burn filter with contents in a platinum crucible, and to deduct the weight of the remaining inorganic residue (less the weight of the filter ash) from that of the albumin.

Peptones may be recognized by first precipitating all albumin by means of boiling the urine acidified by acetic acid, filtering, and adding to the filtrate a few drops of dilute cupric sulphate solution and sodium hydroxide. Peptones will be indicated by the purple color of the biuret reaction.

Blood. The presence of blood in urine manifests itself generally, unless the amount be too slight, by a blood-red or brownish color with a bluish, smoky, or greenish tint, and deposits a red or reddish-brown sediment after standing. As a general rule, all constituents of blood, including the corpuscles, are present, but in some cases hæmoglobin alone has been found.

The tests for blood depend either on the microscope or on chemical changes. By the microscope is examined the deposit which forms on standing; almost unaltered blood corpuscles may be found, or they may be much swollen, decolorized, and deformed; the corpuscles are generally accompanied by blood and fibrin casts.

Whenever blood is present, there are necessarily also albuminoids, which are precipitated by acidulating with acetic acid and boiling, when a brownish coagulum of albumin and hæmatin are precipitated.

Hæmoglobin is also tested for by means of adding to the urine a few drops of freshly prepared tincture of guaiacum, a little ozonized ether, and shaking well. If hæmoglobin is present, the ether assumes a blue color.

Detection of sugar. The sugar found in urine is almost exclusively glucose, $C_6H_{12}O_6$. Traces of sugar, or as much as 0.01 per cent., are said to occur normally in urine, and are of no significance; moreover, it is as yet doubtful whether these traces of sugar are actually present in normal urine. A large amount of sugar is often indicated by a high specific gravity of the urine, which then varies from 1.030 to 1.050; the quantities found vary from mere traces to 10 per cent., the latter quantity, however, being a very rare occurrence, while 3 to 5 per cent. is often found in the urine of persons suffering from diabetes mellitus.

There are many tests by which sugar can be detected. They depend chiefly on the following properties of sugar, viz.: 1, to act as a deoxidizing or reducing agent upon certain metallic oxides (copper, bismuth, silver, mercury) in the presence of alkalies; 2, to produce a yellow or brown color, when in contact with alkalies, slowly in the cold, rapidly on heating; 3, to give a deep red color with picrates in alkaline solution, and a number of different colors with certain phenols in the presence of sulphuric acid; 4, to ferment with yeast; 5, to unite with phenyl-hydrazine to a crystalline compound; 6, to have the power of rotation to the right of the plane of polarization.

The tests for sugar should always be preceded by tests for albumin, which latter, if present, should be removed by coagulation and filtration. Earthy phosphates also interfere with the copper tests sometimes, because they are precipitated by the alkali, and this precipitate may be mistaken either for precipitated cuprous oxide, when no sugar is present, or it may cover the precipitated cuprous oxide to such an extent that this is not recognized, when sugar is present.

To avoid these errors, it is well to render slightly alkaline the urine by a few drops of potash solution, filter after a few minutes, and use this urine for the tests.

Trommer's test. A few drops (2–4) of a 5 per cent. solution of cupric sulphate are added to about 5 to 8 c.c. of urine in a test-tube and then an equal volume of potassium (or sodium) hydroxide solution is added. The alkaline hydroxide precipitates both earthy phosphates and cupric hydroxide, the latter, however, dissolving (especially if sugar be present) in the excess of the alkali, producing a beautiful blue transparent liquid. (If no sugar is present, the color is less blue, but more of a greenish hue.) The liquid is now heated, when, if sugar be present, a yellow precipitate of cuprous hydroxide is formed which subsequently loses its water and becomes the red cuprous oxide, which falls to the bottom or adheres to the sides of the test-tube. (Plate VIII., 5.)

As various organic substances (other than sugar) have a tendency to reduce cuprous oxide at a temperature of 100° C. (212° F.), it is well to set aside a test-tube prepared as above (without heating it) for from six to twenty-four hours. If sugar be present, the formation of cuprous hydroxide will gradually take place, whilst most other orgonic matters do not act upon cupric oxide at ordinary temperature.

In drawing conclusions from the above test, it should be remembered that a change of color does not indicate sugar; that a precipitate of earthy phosphates must not be mistaken for cuprous oxide;

and that substances other than sugar may deoxidize cupric oxide at the temperature of 100° C. (212° F.).

Fehling's test differs from Trommer's test in merely using a previously mixed reagent instead of producing this reagent, as it were, in the urine by adding to it cupric sulphate and an alkaline hydroxide successively. This reagent, known as *Fehling's solution*, or as *alkaline cupric tartrate volumetric solution*, is made by mixing exactly equal volumes of the below-mentioned copper solution and the Rochelle salt solution at the time required.

Copper solution:

Crystallized cupric sulphate	34.64 grammes.
Water, sufficient quantity to make	500 c.c.

Rochelle salt solution:

Potassium sodium tartrate	173 grammes.
Potassium hydroxide	125 "
Water, sufficient quantity to make	500 c.c.

Both solutions are preserved in small well-stoppered bottles, and mixed only at the time needed, because the mixture is apt to decompose when kept some time.

The addition of sodium-potassium tartrate in Fehling's solution prevents the precipitation of cupric hydroxide by the alkaline hydroxide. This action is analogous to the formation of the soluble scale compounds of iron, where the precipitation of ferric hydroxide is also prevented by tartaric or other organic acids.

While Fehling's solution is used chiefly for quantitative determinations, it can also be used to advantage for qualitative tests. This is done by heating about 10 c.c. of Fehling's solution in a test-tube, and adding drop by drop the suspected urine; if the latter contains larger quantities of sugar a yellow or red precipitate of cuprous hydroxide and oxide will be produced very readily; if but small quantities are present, an equal volume of urine may be added to the solution, and the boiling repeated several times before the reaction takes place.

Bötger's bismuth test consists in adding to a mixture of equal volumes of urine and potassium (or sodium) hydroxide solution a few grains of subnitrate of bismuth and boiling for half a minute. If sugar be present, a gray or dark-brown, finally black, precipitate of bismuthous oxide, Bi_2O_2, or of metallic bismuth is formed. If but very little sugar is present, the undecomposed excess of bismuthic nitrate (or bismuthic hydroxide) mixes with the metallic bismuth, imparting to it a gray color; the test should then be repeated with a smaller amount of the bismuth salt. (Plate VIII., 6.)

The above test may be somewhat modified by using a bismuth solution, instead of the powder. The solution known as *Nylander's reagent* is made by dissolving 2 grammes of bismuth subnitrate, 4 grammes of Rochelle salt, and 10 grammes of sodium hydroxide in 90 c.c. of water, and filtering. One-half c.c. of this solution is heated with about 5 c.c. of urine, when, in the presence of sugar, a brown or black precipitate will form after a few minutes.

If the urine contains hydrogen disulphide (sometimes produced by decomposition of certain urinary constituents), black bismuth sulphide will be formed, which may be mistaken for metallic bismuth; albumin itself may be the cause of the formation of alkaline sulphides: the previous complete separation of albumin is therefore indispensable.

Moore's or *Heller's test* is made by heating urine with about one-fourth of its volume of solution of potassium hydroxide. In the presence of sugar the color of the mixture will deepen to a dark yellow or brown, and the depth of color is a fair indication of the quantity of sugar present. In case but a slight change takes place in color, it is well to compare it with that of an unchanged specimen of the urine.

The *fermentation test* is based upon the decomposition of sugar by the action of yeast with generation of carbon dioxide. The test is made by adding to about 50 or 100 c.c. of urine (contained in a large test-tube or small flask) a few grammes of common yeast. The vessel containing the urine is provided with a perforated cork, through which is passed one limb of a bent glass tube, long enough to reach nearly to the bottom of the vessel, which should be completely filled with urine. Under the second limb of the bent glass tube is placed a beaker.

The apparatus thus prepared is placed in a room having a temperature of about 22°–28° C. (72°–82° F.). If sugar be present, fermentation will commence within twelve hours, and will manifest itself by the formation of carbon dioxide, which will force a portion of the fluid through the bent tube into the beaker placed there for its reception.

The disadvantages of this process are the length of time required for its performance, the unreliability of the ferment, and the fact that small quantities of sugar (less than 0.5 per cent.) evolve so little carbon dioxide that a doubt may be felt as to the presence of sugar at all.

Picric acid test for sugar. It has been mentioned above that picric acid serves as an excellent reagent for albumin; in the presence of alkalies it may also be used to advantage as a reagent for sugar. Urine is mixed with a few drops of a saturated aqueous solution of picric acid, a little caustic potash is added and gently heated; a marked reddish or reddish-brown coloration, due to the formation of picramic acid, $H.C_6H_2.NH_2.(NO_2)_2O$, indicates sugar. A reddish color which appears without heating the mixture and which disappears completely within twenty minutes indicates the presence of *kreatinin.* A portion of the reddish liquid heated will turn more intensely red if sugar is also present.

Molisch's test. This is made by adding to urine a few drops of a 10 per cent. alcoholic solution of either thymol, menthol, or alpha-naphthol. Into the inclined test-tube about 2 c.c. of concentrated sulphuric acid are then poured so as to form a layer below the urine. At the zone of contact a color is produced which is red with thymol and menthol, violet with greenish borders with alpha-naphthol. Traces of glucose are shown by these tests.

Phenyl-hydrazine test is made by heating to boiling a mixture of equal volumes of urine and potassium hydroxide solution, to which a few drops of phenyl-hydrazine have been added. In the presence of sugar the mixture assumes an intense yellow or orange color. Upon supersaturating the cooled mixture with acetic acid a precipitate of golden yellow, needle-shaped crystals of phenyl-dextros-azon is formed. The test has the advantage that glucose is the only substance likely to occur in urine, which forms these crystals.

Quantitative estimation of sugar. By far the best method is the decomposition of a copper solution of a known strength, and Fehling's solution prepared as stated above, answers this purpose well.

1000 c.c. of Fehling's solution, containing 34.64 grammes of crystallized cupric sulphate, $CuSO_4.5H_2O$, are decomposed by 5 grammes of grape-sugar, or 1 c.c. of solution by 0.005 of grape-sugar.

To make the quantitative determination, operate as follows: 10 c.c. of Fehling's solution are poured into a porcelain dish of about 200 c.c. capacity, placed over a flame. The copper solution is diluted with about 40 c.c. of water, and heated to boiling; to the boiling liquid, urine (which has been previously diluted with 9 parts of water) is added from a burette very gradually, until the blue color of the solution has disappeared, and there remains, upon subsidence of the cuprous oxide, an almost colorless, clear liquid. A filtered portion of this liquid, acidified with hydrochloric acid, should not give a reddish-brown precipitate with potassium ferrocyanide (a precipitate would show that all copper had not been precipitated, and that more urine was needed), whilst a second portion of the filtered fluid should not produce a red precipitate on boiling with a few drops of Fehling's solution (a precipitate would indicate that too much urine had been added, in which case the operation has to be repeated).

The calculation of the amount of sugar present is easily made. 10 c.c. of Fehling's solution are decomposed by 0.05 gramme of sugar; this quantity must, therefore, be contained in the number of c.c. of urine used. Suppose 30 c.c. of urine, diluted with 9 parts of water, or 3 c.c. of pure urine, have been required to decompose the 10 c.c. of Fehling's solution, then 3 c c. of urine contain of grape-sugar 0.05 gramme, or 100 c.c. of urine 1.666 grammes, according to the proportion:

$$3 : 0.05 :: 100 : x$$
$$x = 1.666.$$

If the urine contains but very little sugar, it may be used directly without diluting it, or instead of diluting it with 9 parts of water, it may be diluted with 4 volumes or with an equal volume of water.

Determination by fermentation. The fermentation test above described can be used for quantitative determination of sugar, provided the quantity present is not less than 0.5 per cent., when the results are fairly accurate. The determination is made by observing carefully the specific gravity of the urine at the same temperature before and after fermentation. The decomposition of the sugar causes the specific gravity to become less, and every degree of the urinometer indicates 0.219 per cent. of sugar. If, for instance, urine showed a specific gravity of 1032 before, and 1022 after fermentation, the quantity of sugar present is 10 times 0.219, or 2.19 per cent. The yeast to be used for the experiment should be well washed upon a filter with pure water, and the urine quickly filtered before taking its specific gravity after fermentation has taken place.

Experiment 77. Determine the amount of sugar in urine by the methods described above. If no suitable urine is to be had, add some glucose to urine and use this solution.

Detection of bile. The presence of bile in urine is generally indicated by a decided color, which varies from a deep brownish-red to a dark brown; the foam of such urine (produced by shaking) has a distinct yellow color, and a piece of filtering-paper or a piece of linen dipped into the urine assumes a yellow color, which does not disappear on drying.

The further detection of bile depends upon the reactions of the biliary coloring matters or biliary acids; it frequently happens, however, that the pigments are present, whilst the acids are not.

Gmelin's test for biliary coloring matters has been considered already, and may be applied to urine either by allowing a small quantity of nitric acid, containing some nitrous acid, to flow down the sides of a test-tube (containing the urine) in such a manner that the two fluids do not mix, or by placing upon a porcelain plate a few drops of the urine, near it a few drops of nitric acid, to which one drop of sulphuric acid has been added, and allowing the two liquids to approach gradually. In both cases (if bile pigment is present) a play of color is seen at the point of union between the two fluids, the colors changing from green to blue, violet-red, and yellow or yellowish-green. While the appearance of the green at the beginning is indispensable to prove the presence of bile, the presence of all the other colors is not essential. (Plate VIII., 7.)

The above test may be made in a somewhat modified form by mixing the urine with a concentrated solution of sodium nitrate, and pouring down the sides of the test-tube concentrated sulphuric acid in such a manner as to form two distinct layers; the colors are seen at the point of contact as above.

If the urine be very dark in color, it should be diluted with water before applying the above tests.

Ultzmann's test for bile pigment is made by mixing 10 c.c. of urine with 3 or 4 c.c. of potassium hydroxide solution (1 in 3 of water), and supersaturating with hydrochloric acid; the mixture assumes a beautiful emerald-green color after some time.

Pettenkofer's test for biliary acids is made by dissolving a few grains of cane-sugar in urine contained in a test-tube, and allowing some concentrated sulphuric acid to trickle down the side of the inclined test-tube; a purple band is seen at the upper margin of the acid, and on slightly shaking the liquid becomes at first turbid, then clear, and almost simultaneously it turns yellow, then pale cherry-red, dark carmine-red, and finally a beautiful purple violet. The temperature must not be allowed to rise much above 38° C. (100° F.) (Plate VIII., 8.)

As many substances (other than biliary acids) show a similar reaction, it is often necessary to separate the bile acids by the process described in connection with the consideration of bile itself.

In case the quantity of biliary constituents is so small that they cannot be noticed by the tests mentioned, the urine should be shaken with about one-fourth of its volume of chloroform, which dissolves the biliary matters. Some of this solution is dropped upon blotting paper, and after evaporation a drop of red fuming nitric acid is placed in the centre of the remaining stain, when concentric color rings appear. The second portion of chloroform solution is evaporated and the residue used for making the reactions as described above.

Diazo-reaction. Some abnormal constituent (which has not yet been isolated) is found in the urine of persons suffering from typhoid fever. The presence of this unknown substance is indicated by a very characteristic reaction with diazo-benzol-sulphonic acid, which compound is produced by the action of nitrous acid on sulphanilic acid. Two solutions are required: *a.* 2 grammes of sulphanilic acid dissolved in a mixture of 50 c.c. of hydrochloric acid and 1000 c.c. of water; *b.* A 0.5 per cent. solution of sodium nitrite. To perform the reaction 50 parts of *a* and 1 part of *b* are mixed, and equal volumes of the reagent and of urine are mixed in a test-tube and saturated with ammonia. In those cases in which the reaction is positive the solution assumes a carmine-red color, which, on shaking, must also be visible in the foam. If the test-tube is allowed to stand twenty-four hours, a greenish precipitate is formed. Normal urine, thus treated, shows a deep yellow or orange color; the precipitated phosphates as well as the foam are colorless.

While the reaction is also found in some cases of measles, sepsis, scarlet fever, etc., yet its constant and early presence in typhoid fever and its presence in severe cases of pulmonary tuberculosis make the reaction of considerable diagnostic and prognostic importance in these diseases.

Acetone and diacetic acid. Both of these substances appear in considerable quantities in the urine when there is marked destruction of the protoplasm of the body; they are more especially found in cases of high fever, in some cases of cancer, and in severe forms of diabetes. Large quantities of acetone appear in the urine during disturbances of digestion and in intestinal diseases.

Diacetic acid, $CH_3.COCH_2.CO_2H$, is recognized by means of Gerhard's ferric chloride reaction. A solution of ferric chloride added to the urine produces a gray precipitate of ferric phosphate; upon the further addition of the iron solution a deep bordeaux color appears. The foam produced on shaking the test-tube is reddish-violet. On the addition of sulphuric acid the red color disappears. Diacetic acid readily decomposes with the formation of acetone.

Acetone is recognized in the following manner: 500 c.c. of urine are acidified with a few drops of hydrochloric acid and distilled. To the distillate a few drops of iodine solution (1 iodine, 2 potassium iodide, 100 water), and of potassium hydroxide are added. If acetone is present a characteristic yellowish-white precipitate of iodoform is formed.

Urinary deposits (*sediments*). Normal urine is always clear, but occasionally, and particularly in abnormal conditions, it is turbid.

Urine may be turbid when passed, and this indicates an excess of mucus, or the presence of renal epithelium, pus, blood, chyle, semen, bile, or phosphate or urate of sodium in excess, etc. A turbidity subsequent to the passage of the urine is generally due to the precipitation of phosphates or urates, or it may result from fermentation or decomposition. Either of the substances named will form a deposit on standing.

When such a deposit is to be examined, a few ounces of the urine should be set aside for several hours in a tall, narrow, cylindrical glass; when the sediment has collected at the bottom, the supernatant urine may be decanted, or the sediment may be taken out by means of a pipette for examination.

Sediments are either organized or unorganized. To the first belong: mucus, blood, pus, urinary casts, epithelium, spermatozoids, fungi, infusoria, etc.; to the second belong: uric acids, urates, calcium oxalate, phosphate, or carbonate, magnesium-ammonium phosphate, cystin, hippuric acid, etc.

The chemical examination of any urinary sediment should always be preceded by a microscopical examination, which latter is in many cases the only way of determining the nature of the sediment, especially of the organized substances. Most of the unorganized and either crystalline or amorphous sediments may be easily recognized by chemical means.

Urates of ammonium, calcium, and *sodium* dissolve on heating the urine, and are reprecipitated on cooling. The murexid test is used in addition.

Phosphates of calcium or *ammonium-magnesium* dissolve in acetic acid, and ammonium molybdate dissolved in nitric acid produces a yellow precipitate on heating.

Calcium oxalate is insoluble in acetic, but soluble in hydrochloric acid, from which solution it is reprecipitated on neutralizing with ammonia.

Uric acid is not dissolved by heat, nor by acetic or hydrochloric acid, but dissolves on the addition of caustic potash and burns on platinum foil without leaving a residue; it is recognized by the murexid test.

Cystin is insoluble in water and alcohol, but soluble in mineral acids and in caustic alkalies; from either solution it is reprecipitated by neutralizing. Cystin contains 26 per cent. of sulphur, which causes the formation of black sulphide of lead when cystin is boiled with caustic potash to which a few drops of solution of lead acetate have been added.

Urinary calculi are solid deposits of larger or smaller size formed from the urine within the tracts (kidneys, ureter, bladder, and urethra).

The chemical composition of the calculi is generally that of either of the above-named unorganized sediments, and their nature can easily be determined by using the following method:

Make a section through the centre of the calculus, scrape some of the substance off, powder it finely, and heat some of it on platinum foil. It may either burn away completely (uric acid, urate of ammonium, cystin, xanthin) or may be partially combustible (urates or oxalates), or may be incombustible (chiefly phosphates). A slight blackening occurs generally, even in heating a calculus consisting of incombustible matter, and is due to the presence of traces of organic urinary constituents.

If completely combustible, digest a little of the powder with dilute hydrochloric acid; cystin and xanthin are dissolved, uric acid remains undissolved. Apply murexid test for uric acid, the above-mentioned lead test for cystin, and for xanthin test by dissolving a little of the calculus in nitric acid and evaporating to dryness, when in the presence of xanthin a bright-yellow residue will be left, which becomes violet-red when treated with caustic potash. In case uric acid has been found, it may be in combination with ammonia, which may be verified by heating the powder with a little caustic potash, when ammonia gas is liberated, which may be recognized by its action on red litmus-paper, odor, etc.

If partially combustible or incombustible, digest some of the powder with dilute hydrochloric acid. If it dissolves completely, uric acid is not present. If a residue be left, apply the murexid test. To a portion of the solution add ammonium molybdate and heat; a yellow precipitate indicates phosphoric acid. To another portion add ammonia water and then excess of acetic acid; a white pulverulent residue indicates calcium oxalate, which can be verified by igniting some of the calculus and adding a drop of acid, when effervescence will be noticed, the oxalate having been converted into a carbonate by the ignition ; the solution thus obtained can be tested for calcium by the addition of water of ammonia and ammonium oxalate. In case phosphoric acid has been found, this is present either as a calcium or magnesium-ammonium salt. To distinguish between them, neutralize the solution of the powder in hydrochloric acid with ammonia, add acetic acid and ammonium oxalate; a white precipitate indicates calcium; if no precipitate is produced, supersaturate with ammonia, when the crystalline magnesium-ammonium phosphate will gradually form.

Most common are calculi of uric acid ; often met with are those of urates, phosphates, and oxalates ; rarely, however, those of xanthin and cystin.

Microscopical examination of urinary sediments. The chemical examination of any urinary sediment should always be preceded by a microscopical examination, which latter is in many cases the only way of determining the nature of the sediment, especially of the organized substances.

Fig. 44, A–O, shows the principal sediments found in, or produced from, urine, as seen with a magnifying power of 200 diameters.

A. *Uric acid* occurs in many different forms, mostly in rhombic plates, with rounded obtuse angles, often joined into rosettes. Uric acid is found almost invariably colored red or reddish-brown, which generally distinguishes it from other sediments. The crystals or clusters of crystals are often large enough to be seen by the naked eye, and are then known by the terms "sand," "gravel," or "red-pepper grains."

B. *Ammonium acid urate* is found, generally associated with amorphous or crystalline phosphates, in urine which has become alkaline. The crystalline globules are generally covered with spinous excrescences, which give them the characteristic "thorn-apple" appearance.

C. *Sodium urate* forms generally a part in the pulverulent, heavy, variously tinted deposit of the mixed urates known as "brickdust" or "lateritious" sediment. It occurs either in fine amorphous granules which cannot be distinguished microscopically from other amorphous sediments or in a crystalline form as shown in the figure.

D. *Urea nitrate* crystallizes readily in large six-sided plates on the addition of nitric acid to urine.

E. 1, *Leucin*, or amido-caproic acid, $C_6H_{11}(NH_2)O_2$; and 2, *Tyrosin*, $C_9H_{11}NO_3$, are but rarely met with in urinary deposits. Leucin is found either as rounded lumps, showing but little crystalline structure, or as spherical masses, exhibiting fine radial striation. Tyrosin appears generally in fine, long, silky needles, forming bundles or rosettes.

F. *Cystin* occurs occasionally as a grayish, crystalline deposit, forming transparent six-sided plates; it also occurs in calculi. The latter may be recognized by the above-mentioned chemical properties or by dissolving a little in hydrochloric acid and neutralizing with ammonia, when cystin is reprecipitated and shows the characteristic six-sided plates under the microscope.

G. *Magnesium-ammonium phosphate*, or triple phosphate, $MgNH_4PO_4.6H_2O$, is found generally in triangular prisms with bevelled ends, as shown in 1, but sometimes also in star-shaped, feathery crystals, represented in 2.

H. *Calcium phosphate*, $Ca_3(PO_4)_2$, is most frequently found in amorphous globules, but also crystallized either in prisms, 1, or in "wedge-shaped" crystals, 2.

I. *Calcium oxalate*, CaC_2O_4, occurs either in quadratic octohedra with brilliant refraction, 1, or sometimes in the shape of "dumb-bells," 2.

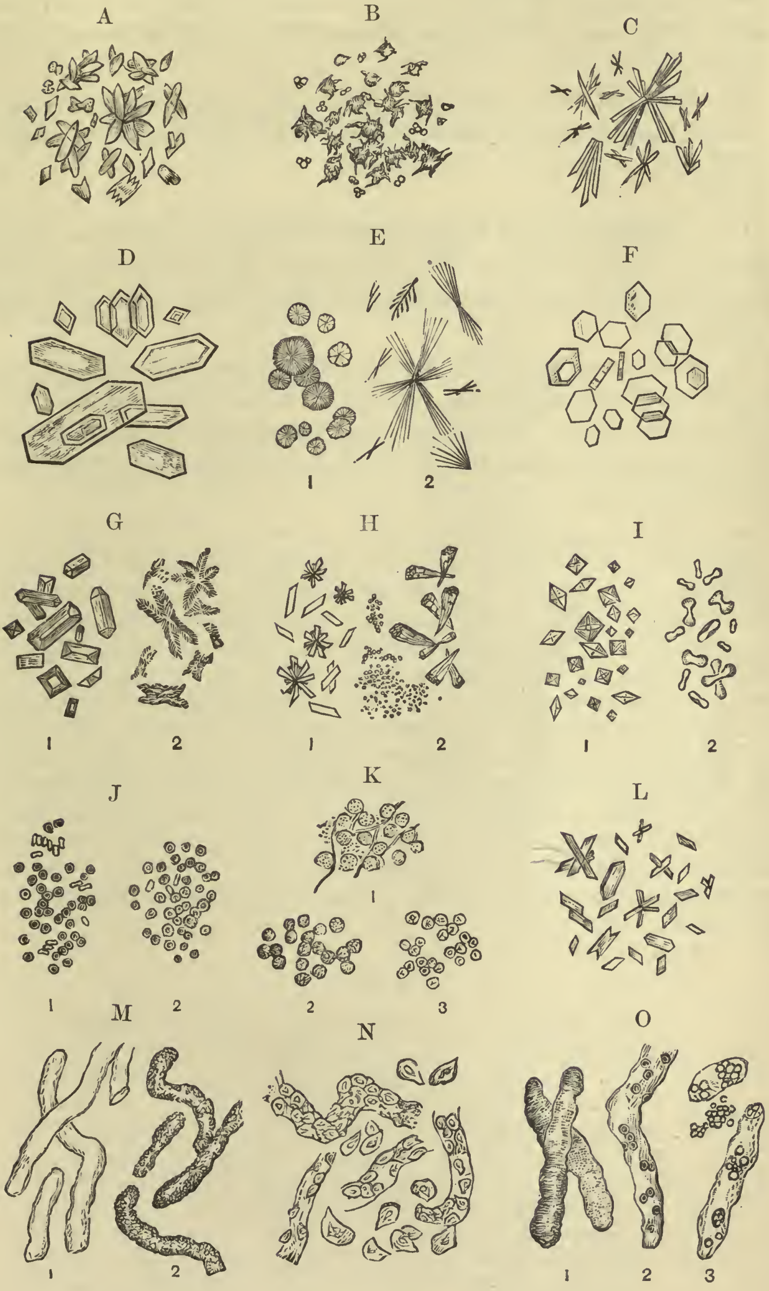
J. *Blood corpuscles* appear under the microscope as reddish, circular disks, sometimes laid together in strings. If seen in profile, they appear biconcave. 1, shows the corpuscles in a fresh condition; 2, as generally seen in urine.

K. *Mucus and pus* are often difficult to distinguish from each other under the microscope, as they both appear as little granular globules, varying somewhat in appearance with the reaction of the urine. Pus is rendered slimy, ropy, viscid, and tenacious by the addition of caustic potash. 1, shows globules of mucus; 2, of pus; and 3, of pus treated with acetic acid, which clears up the granular globules with the appearance of a nucleus.

L. *Hæmin crystals.* The formation of these crystals often serves to recognize blood, and is accomplished by mixing the latter on a glass slide with a trace of sodium chloride and a drop of glacial acetic acid and warming gently, when the characteristic crystals will appear. By repeating the process several times, larger and better-developed crystals are obtained.

M. 1, *Hyaline casts;* 2, *Granular casts.* Urinary casts are tube-like cylinders, often found together with blood and pus corpuscles, or

FIG. 44.



Urinary sediments.

holding in their substance or walls epithelial cells, mucous corpuscles, and fat globules. Hyaline casts are distinguished by their transparent appearance, while granular casts show a more or less granular surface.

N. *Epithelial casts and cells.* According to the origin (vagina, urethra, bladder, etc.) of these bodies, they differ somewhat, and it is difficult to recognize with certainty the source whence they are derived.

O. 1, *Waxy casts;* 2, *Casts with blood corpuscles;* 3, *Casts with fat globules.* Waxy casts resemble hyaline casts, but are less transparent. Casts containing blood corpuscles or fat globules are generally easily recognized.

In addition to the above-mentioned urinary deposits there may also be found various kinds of fungi, vibriones, spermatozoids, hair, or even such foreign matters as fibres of cotton, wool, or silk, with the characteristic appearance of which the student should familiarize himself thoroughly.

QUESTIONS.—551. What points are to be considered, and what substances determined, in the analysis of normal and abnormal urine? 552. What is the color of urine, and what are the chief causes influencing the color? 553. What is the specific gravity of healthy urine, how is it determined, and how is the total amount of solids approximately calculated from the specific gravity? 554. Describe the different tests by which albumin may be recognized, and state the precautions necessary in making these tests. 555 How may the quantity of albumin in urine approximately and how accurately be determined? 556. Describe the various tests for sugar. On what principles are they based? 557. How is sugar determined quantitatively? 558. By what tests are biliary pigments and acids recognized in urine? 559. What is the nature of urinary sediments, and by what means are they recognized? 560. What are urinary calculi generally composed of, and by what simple tests can their nature be determined?

APPENDIX.

TABLE OF WEIGHTS AND MEASURES.

Measures of length.

1 millimeter	=	0.001	meter	=	0.0394	inch.
1 centimeter	=	0.01	meter	=	0.3937	inch.
1 decimeter	=	0.1	meter	=	3.9371	inches.
1 meter				=	39.3708	inches.
1 decameter	=	10	meters	=	32.8089	feet.
1 hectometer	=	100	meters	=	328.089	feet.
1 kilometer	=	1000	meters	=	0.6214	mile.
1 yard or 36 inches				=	0.9144	meter.
1 inch				=	25.4	millimeters.

Measures of capacity.

1 milliliter	=	1 c.c.	=	0.001	liter	=	0.0021	U. S. pint.
1 centiliter	=	10 c.c.	=	0.01	liter	=	0.0211	U. S. pint.
1 deciliter	=	100 c.c.	=	0.1	liter	=	0.2113	U. S. pint.
1 liter	=	1000 c.c.				=	1.0567	U. S. quart.
1 decaliter			=	10	liters	=	2.6418	U. S. gallons.
1 hectoliter			=	100	liters	=	26.418	U. S. gallons.
1 kiloliter			=	1000	liters	=	264.18	U. S. gallons.
1 U. S. gallon						=	3785.3	c.c.
1 imperial gallon						=	4543.5	c.c.
1 minim						=	0.06	c.c.
1 fluidrachm						=	3.70	c.c.
1 fluidounce						=	29.57	c.c.
1 liter						=	33.81	fluidounces.

Weights.

1 milligram	=	0.001	gramme	=	0.015	grain	Troy.
1 centigram	=	0.01	gramme	=	0.154	grain	Troy.
1 decigram	=	0.1	gramme	=	1.543	grain	Troy.
1 gramme				=	15.432	grains	Troy.
1 decagram	=	10	grammes	=	154.324	grains	Troy.
1 hectogram	=	100	grammes	=	0.268	pound	Troy.
1 kilogram	=	1000	grammes	=	2.679	pounds	Troy.
1 grain Troy				=	0.0648	gramme.	
1 drachm Troy				=	3.888	grammes.	
1 ounce Troy				=	31.103	grammes.	
1 ounce avoirdupois				=	28.350	grammes.	
1 pound avoirdupois				=	453.592	grammes.	

Commercial weights and measures of the U. S. A.

1 pound avoirdupois = 16 ounces.
1 ounce = 437.5 grains.
1 gallon = 231 cubic inches.
1 gallon = 4 quarts = 8 pints.
1 pint of water weighs 7291.2 grains at a temperature of 15.6°.

Troy weight.

1 drachm = 60 grains.
1 ounce = 8 drachms = 480 grains.

TABLE OF ELEMENTS.

	Symbol.	Atomic weight.		Symbol.	Atomic weight.
Aluminum	Al	27.04	Molybdenum	Mo	95.9
Antimony	Sb	119.6	Nickel	Ni	58.6
Arsenic	As	74.9	Nitrogen	N	14.01
Barium	Ba	136.9	Osmium	Os	190.3
Beryllium[1]	Be	9.03	Oxygen	O	15.96
Bismuth	Bi	208.9	Palladium	Pd	106.35
Boron	B	10.9	Phosphorus	P	30.96
Bromine	Br	79.76	Platinum	Pt	194.3
Cadmium	Cd	111.5	Potassium	K	39.03
Cæsium	Cs	132.7	Rhodium	Rh	102.9
Calcium	Ca	39.91	Rubidium	Rb	85.2
Carbon	C	11.97	Ruthenium	Ru	101.4
Cerium	Ce	139.9	Samarium	Sm	149.62
Chlorine	Cl	35.37	Scandium	Sc	43.97
Chromium	Cr	52.0	Selenium	Se	78.87
Cobalt	Co	58.6	Silicon	Si	28.3
Columbium[2]	Cb	93.7	Silver	Ag	107.66
Copper	Cu	63.18	Sodium	Na	23.0
Didymium[3]	Di	142.0	Strontium	Sr	87.3
Erbium	Er	166.0	Sulphur	S	31.98
Fluorine	F	19.0	Tantalum	Ta	182.0
Gallium	Ga	69.9	Tellurium	Te	125.0
Germanium	Ge	72.3	Terbium	Tb	159.1
Gold	Au	196.7	Thallium	Tl	203.7
Hydrogen	H	1.0	Thorium	Th	231.9
Indium	In	113.6	Tin	Sn	118.8
Iodine	I	126.53	Titanium	Ti	48.0
Iridium	Ir	192.5	Tungsten	W	183.6
Iron	Fe	55.88	Uranium	U	238.8
Lanthanum	La	138.2	Vanadium	V	51.1
Lead	Pb	206.4	Ytterbium	Yb	172.6
Lithium	Li	7.01	Yttrium	Yt	88.9
Magnesium	Mg	24.3	Zinc	Zn	65.1
Manganese	Mn	54.8	Zirconium	Zr	90.4
Mercury	Hg	199.8			

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[1] Also called glucinum.

[2] Also called niobium.

[3] Composed of neo- and praseo-didymium.

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